

METHODS OF FIBER SURFACE GRAFTING
FOR
INTERPHASE DESIGN AND TAILORED COMPOSITE RESPONSE

By

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This dissertation is dedicated to my wonderful and irreplaceable wife, Jesyca.
Her unyielding love and support buoyed the many failures and inspired the few successes.

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TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS	iii
LIST OF TABLES	viii
LIST OF FIGURES	xi
ABSTRACT	xvii
 CHAPTERS	
1 INTRODUCTION	1
Polymer-Matrix Composites	1
Fiber/Matrix Interfacial Properties	4
Interfaces and Interphases	8
Experimental Summary	10
2 BACKGROUND	13
Fiber/matrix Adhesion	15
Characterization of Interfacial Properties	17
Surface Modification of UHMPE Fibers	20
Plasma surface modification	21
Radiation-induced grafting	33
Composite Impact Performance	36
Impact Strength	38
Tailored Interphases for Optimum Composite Performance	47
3 SURFACE MODIFICATION OF ULTRA HIGH MODULUS POLYETHYLENE FIBERS BY γ -RADIATION INDUCED GRAFTING	58
Introduction	58
Experimental	62
Fibers	62
Polymer Matrices	62
Composites	63

Characterization.....	63
Results and Discussion.....	65
Characterization of Fibers.....	65
FTIR.....	65
ESCA.....	66
Tensile properties of UHMPE fibers.....	68
Polystyrene Composite Properties.....	70
S/BA/CHM Terpolymer Composite Properties.....	77
Conclusions.....	86
4 CHARACTERIZATION OF UHMPE FIBER/MATRIX ADHESION BY DYNAMIC MECHANICAL SPECTROMETRY.....	88
Introduction.....	88
Experimental.....	92
Materials.....	92
Characterization.....	93
Results and Discussion.....	95
Tensile Properties of Polystyrene Composites.....	95
Tensile Properties of Terpolymer Composites.....	96
Contact Angle Measurements of HDPE Films.....	97
DMS and Three Phase Modeling of Composites.....	99
Conclusions.....	112
5 ANNEALING OF ULTRA-HIGH MODULUS POLYETHYLENE FIBERS: TENSILE PROPERTIES AND IMPLICATIONS OF FIBER MORPHOLOGY.....	115
Introduction.....	115
Experimental.....	119
Fibers.....	119
Annealing Treatments.....	120
Differential Scanning Calorimetry.....	120
Tensile Tests.....	120
X-Ray Diffraction.....	121
SEM of the Fiber Tensile Fracture Surfaces.....	121
Results and Discussion.....	121
Characterization of Annealed UHMPE Fibers.....	121
Implications of the Morphology of UHMPE Fibers.....	128
Fracture Analysis by Scanning Electron Microscopy.....	134
Conclusions.....	136
6 HYDROPEROXIDE INITIATED GRAFTING OF POLY(STYRENE-STAT- ACRYLONITRILE) ONTO ULTRA-HIGH MODULUS POLYETHYLENE FIBERS.....	139

Introduction	139
Experimental	142
Grafting by Hydroperoxide Surface Modification	142
Characterization of UHMPE Fibers and SAN Grafts	143
Results and Discussion	145
Thermal and Mechanical Properties of UHMPE Fibers	145
Surface Analysis of the UHMPE Fibers by ESCA	148
Atomic Force Microscopy of UHMPE Fibers	153
Conclusions	163
7 TAILORED COMPOSITE RESPONSE THROUGH FIBER SURFACE GRAFTING	165
Introduction	165
Experimental	173
Materials	173
Interphase Design Using the Shear Lag Model with Interphase	174
Styrene/Acrylonitrile/Butyl Acrylate Copolymer Synthesis	177
Characterization of S/AN/BA copolymers	180
Grafting UHMPE Fabrics by Hydroperoxide Surface Modification	181
Composite Fabrication	184
Results and Discussion	190
S/AN/BA Copolymers	190
S/AN/BA Grafts	195
S/AN/BA-grafted UHMPE Fiber-Reinforced Composites	200
Conclusions	217
8 CONCLUDING REMARKS	221
Implications of the Research	221
Future Directions	226
APPENDIX COMMON ABBREVIATIONS AND ACRONYMS	229
LIST OF REFERENCES	232
BIOGRAPHICAL SKETCH	241

LIST OF TABLES

<u>Table</u>	<u>page</u>
1-1. Typical Mechanical Properties Of High Performance Fibers.	3
1-2. Typical ILSS Ranges of High Performance Fibers.	8
2-1. Summary of UHMPE Surface Treatments and Interfacial Strengths.	19
2-2. Summary of UHMPE Fiber Surface Grafting Methods and Monomers.	32
2-3. Effect of Improved Surface Treatment on the Impact Strength of UHMPE-Fiber-Reinforced Composites.	38
3-1. UHMPE Fiber Composite Nomenclature.	63
3-2. Tensile Properties of Polystyrene Composites.	73
3-3. Tensile Properties of S/BA/CHM Terpolymer Composites.	80
4-1. Randomly Oriented, UHMPE Fiber-Reinforced Composite Nomenclature.	93
4-2. Tensile Properties of Polystyrene Composites.	96
4-3. Tensile Properties of S/BA/CHM Terpolymer Composites.	97
4-4. Contact Angle of HDPE Films Measured by the Captive Bubble Technique.	99
5-1. Tensile Properties of Annealed UHMPE Fibers.	125
5-2. Enthalpy of Melting (J/g), ΔH_m , of UHMPE Fibers after Annealing at 137°C and 140°C.	126
5-3. WAXD Results for the Annealing of UHMPE Fibers.	127
6-1. Summary of UHMPE fiber surface grafting methods and monomers.	140
6-2. Tensile Properties of UHMPE Single Fibers.	148
6-3. Enthalpy of melting (J/g) for UHMPE fibers.	148

6-4. Quantitative ESCA analysis of UHMPE Fibers	152
6-5. Molar mass distribution of SAN homopolymer and predictions of SAN grafts based on AFM.....	162
7-1. ILSS Ranges of Typical High Performance Fibers	166
7-2. Chemical Products for the Synthesis of Epoxy Matrix	174
7-3. The S/AN/BA terpolymer compositions and corresponding thermal and mechanical properties evaluated during multiple iterations towards the final Mid-Tg composition.....	192
7-4. Results from Elemental Analysis of S/AN/BA Terpolymers (provided by the Department of Chemistry, University of Florida).....	193
7-5. The Feed and Final Compositions Determined by Elemental Analysis along with the Relevant Mechanical Properties of S/AN/BA Terpolymers.....	195
7-6. Bulk and Surface Atomic Concentrations of the S/AN/BA Terpolymers Determined by Elemental and ESCA Analysis.....	197
7-7. ESCA Surface Analysis of S/AN/BA-grafted UHMPE Fibers and Terpolymers for the Determination of the Grafting Efficiency.....	197
7-8. Effect of Hydroperoxidation Temperature on the Grafting Efficiency.....	200
7-9. DSC and Density Measurements of UHMPE-fiber Reinforced Epoxy Composites for the Determination of v_f and v_v	203
7-10. Flexural properties of UHMPE fiber-reinforced epoxy composites ($E_m =$ 3.24 GPa)	206
7-11. Effect of Grafting Efficiency of Mid-Tg S/AN/BA-grafted UHMPE Fibers on the Flexural Properties of Fiber-reinforced Composites.....	207
7-12. ILSS of UHMPE Fiber-reinforced Composites.....	211
7-13. The Tensile Yield Strength and the Shear Strength of the Matrix and Interphase Terpolymers Calculated According to the von Mises Criterion along with the ILSS of the S/AN/BA-grafted UHMPE/epoxy Composites.....	212
7-14. Solubility parameters of the S/AN/BA terpolymers and the epoxy matrix calculated from group molar attraction constants.....	214
7-15. Effect of Grafting Efficiency on the ILSS of Mid-Tg S/AN/BA-grafted UHMPE Fiber-reinforced Composites.....	214

7-16. Impact Strength of UHMPE Fiber-reinforced Composites.....	216
7-17. Impact Strength Decreases with Conventional Oxygen-plasma Treatment.	216
7-18. Effect of grafting efficiency on the impact strength of UHMPE/Epoxy composites.....	216

LIST OF FIGURES

Figure	page
1-1. Reinforcement efficiency of selected high-performance-fiber/epoxy composites. 1, 3	6
2-1. SEM micrographs of (a) PT Spectra® 1000 {conditions: 5 keV, magnification x 1700, Au-Pd coating (9 kV, 30s, 13 Pa)} and (b) PT Spectra® 1000 {conditions: 5 keV, magnification x 1700, Au-Pd coating (9 kV, 180s, 13 Pa)} highlighting the damage that can be caused by excessive coating time. 28	25
2-2. Schematic diagram illustrating the approach of the crack (top) and the possible failure mechanisms as the interfacial strength increases. When the interfacial strength is low, debonding occurs by the Cook-Gordon mechanism (middle image), and under conditions of high interfacial shear strength, the crack propagates perpendicular to the fiber axis. 6, 51	40
3-1. FTIR/photoacoustic spectroscopy of UHMPE fibers irradiated in chloroform with no monomer present (top spectra) and the subtraction result of poly(butyl acrylate)-grafted and irradiated UHMPE fibers (bottom spectra).	67
3-2. High-resolution ESCA C(1s) spectra of (1) as-received, (2) gamma-irradiated in chloroform, and (3) poly(butyl acrylate)-grafted UHMPE fibers. The additional peak in (3) indicates the chemical shift in C(1s) binding energy associated with the ester groups in PBA surface grafts.	69
3-3. Tensile properties of untreated, gamma-irradiated in chloroform only (denoted 'GAMMA'), PCHM-grafted, PBA-grafted and plasma-treated UHMPE (Spectra® 1000) fibers.	71
3-4. The engineering stress-elongation response of polystyrene composites.	72
3-5. SEM micrograph of tensile fracture surface of PS/R4/UNPE composite (magnification x780).	75

3-6. SEM micrograph of tensile fracture surface for PS/R4/CHMPE composite (magnification x780).	75
3-7. SEM micrograph of tensile fracture surface for PS/R4/PTPE composite (magnification x860).	76
3-8. SEM micrograph of tensile fracture surface for PS/R4/BAPE composite (magnification x860).	76
3-9. Tensile energy to break of PS composites.	78
3-10. The engineering stress-percent elongation response of the S/BA/CHM terpolymer composites.	79
3-11. SEM micrograph of tensile fracture surface for TER/R4/UNPE composite (magnification x720).	81
3-12. SEM micrograph of tensile fracture surface for TER/R4/BAPE composite (magnification x720).	81
3-13. SEM micrograph of tensile fracture surface for TER/R4/CHMPE composite (magnification x720)	82
3-14. SEM micrograph of tensile fracture surface for TER/R4/PTPE composite (magnification x780).	82
3-15. Tensile energy to break of terpolymer composites.	84
4-1. Schematic of the contact angle, θ , measured by the captive bubble technique (Note that the image is inverted).	98
4-2. The storage modulus (E') and tan delta temperature profiles of the terpolymer and the TER/R4/CHMPE composite ($v_f = 0.04$, $l_f = 10$ mm).	100
4-3. The measured $\tan \delta$ spectra of the terpolymer composites for the various fiber surface treatments ($v_f = 0.04$, $l_f = 10$ mm).....	102
4-4. The measured $\tan \delta$ spectra of the polystyrene composites for various fiber surface treatments ($v_f = 0.04$, $l_f = 10$ mm).....	104
4-5. The three-phase block model, where the f and m subscripts refer to fiber and matrix attributes, respectively. Volume fraction is denoted by ϕ and the terms K and λ are used to describe the reinforcement efficiency and the amount of matrix material in series, respectively.	105

4-6. The simulated $\tan \delta$ response of the terpolymer composites when λ is fixed ($\lambda = 0.08$).....	108
4-7. The simulated $\tan \delta$ spectra of the polystyrene composites when λ is fixed ($\lambda = 0.08$).	109
4-8. The simulated $\tan \delta$ spectra of the S/BA/CHM terpolymer composites. (K, λ) solutions that yield the best fit with the measured response are tabulated for each fiber surface treatment.	111
4-9. The simulated $\tan \delta$ spectra of polystyrene composites. (K, λ) solutions are tabulated for each fiber surface treatment.....	113
5-1. The DSC thermal response of UHMPE fibers is shown in the top portion of the figure. Indications of polyethylene chain reorganization are observed beginning at 90°C. The onset temperature of melting is equal to 140°C. The bars represent the number of times UHMPE fibers were processed at a particular temperature. Nearly half of the studies, to date, involve processing temperatures above the recommended value of 90°C.....	117
5-2. The tensile strength of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation (n=10).....	122
5-3. The tensile modulus of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation (n=10).....	123
5-4. The percent elongation to failure of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation (n=10).....	124
5-5. A schematic of the microfibrillar morphology of UHMPE fibers. ¹¹⁴	129
5-6. Advancing water contact angles of air-plasma treated UHMPE fibers (Spectra® 900) versus annealing temperature (annealing time=2 hrs). ²²	132
5-7. SEM micrograph of as-received UHMPE fiber after tensile failure (magnification x400).	135
5-8. SEM micrograph of as-received UHMPE after tensile failure (magnification x1500).	135

5-9. SEM micrograph of UHMPE fiber annealed at 137°C for 2 hours (magnification x400).	137
5-10. SEM micrograph of UHMPE fiber annealed at 137°C for 2 hours (magnification x1200).	137
6-1. Tensile properties of UHMPE single filaments (ASTM D2256). "Washed" denotes cleaned in refluxing acetone for 2 hr. and benzene at 70°C for 1.5 hr. The horizontal reference lines denote the average properties of the as-received fibers. The error bars represent one standard deviation of the sample distribution (6-9 samples tested per group).	147
6-2. DSC response curves of SAN-grafted (top curve), HPX-only (middle curve) and as-received (bottom curve) UHMPE fibers. The difference in the enthalpy of melting after the hydroperoxidation and grafting is not statistically significant.	149
6-3. High resolution ESCA-N(1s) spectrum of as-received UHMPE fibers.	150
6-4. High resolution ESCA-N(1s) spectrum of hydroperoxidized UHMPE fibers.	150
6-5. High resolution ESCA-N(1s) spectrum of SAN-grafted UHMPE fibers.	151
6-6. TMAFM™ images of as-received UHMPE fiber. Macrofibrils are 50 nm wide and 15-20 nm in height.	154
6-7. TMAFM™ images of SAN-grafted UHMPE fiber. The textured surface is composed of nodules, 3-12 nm wide and 10-25 nm apart.	156
6-8. 'Hard-Sphere' model of the SAN graft conformation on the surface of UHMPE fibers. The thin horizontal lines represent fully extended polyethylene chains, or microfibrils as proposed by Peterlin, oriented along the fiber axis. ¹¹⁴ The regions containing densely packed and oriented PE chains represent the PE crystallites with an associated long period repeat distance, L. The lines joining adjacent crystallites denote a crystalline bridge. These are also referred to as taut tie molecules according to Peterlin's model. ¹¹⁴ The blank regions between the crystallites, traversed by taut tie molecules, represent the amorphous domains. The SAN grafts are tethered from the amorphous surface domains and assume a random coil conformation, represented as 'hard spheres'.	158
6-9. Root mean square end-to-end distance of a free and a tethered polymer chain with corresponding equations for the determination of the radius of gyration and the polymer molar mass. The mean end-to-end	

distance, r , is expressed in terms of the degree of polymerization, n , the backbone bond length, l , and the fixed bond angle and bond rotation restrictions, θ and Φ , respectively. The mean end-to-end distance is related to the radius of gyration, r_g , by a factor of six. M_S and M_{AN} represent the molar mass of styrene and acrylonitrile, respectively.	161
7-1. Schematic of cross section (top portion) and free body diagram (bottom portion) of composite with interphase.	170
7-2. The effect of interphase thickness on the shear stress at the fiber/interphase margin computed from the shear lag model for three different interphase moduli.	175
7-3. UV/VIS transmission spectra for wash solutions following S/AN/BA hydroperoxidation grafting.	183
7-4. Schematic of the three part mold used to compression mold woven, bidirectional fiber-reinforced composites.	185
7-5. The composition drift associated with terpolymerizations of S/AN/BA copolymers (conversions less than 5%). The numbers 1, 2 and 3 denote the High T _g (T _g = 78°C), Mid T _g (T _g = 38°C) and Low T _g (T _g = -14°C) S/AN/BA terpolymers, respectively.	191
7-6. Tensile stress-elongation response of High-T _g , Mid-T _g and Low-T _g S/AN/BA terpolymers. Note that a break in the percent elongation axis is provided to show the elongation to failure of the Mid-T _g terpolymer. An insert is also included to illustrate the tensile response of the Low-T _g interphase terpolymer.	194
7-7. Thermal response curves for as-received UHMPE fibers and a UHMPE fiber-reinforced epoxy composite sample. The top portion of the figure shows the DSC signal-temperature spectra. The peak is associated with the melting of polyethylene crystallites in the fibers. In the bottom half of the figure, the DDSC-temperature response is shown, which represents the first derivative of the DSC-temperature curve. The DDSC was used to determine the melting onset and completion temperatures. The w_f of fibers was determined using the ratio of ΔH_c and ΔH_f	202
7-8. Flexural response of UHMPE fiber/epoxy composites (plain woven fibers, 7plies).	204
7-9. Effect of grafting efficiency of Mid-T _g S/AN/BA-grafted UHMPE fibers on the flexural response of fiber-reinforced composites (plain woven, 7plies). The grafting efficiency is increased 50% when the hydroperoxidation temperature is raised 20°C.	208

7-10. Typical short beam shear-response curves for UHMPE fiber-reinforced composites.....	210
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The objective of this research was to develop methods of fiber surface grafting for interphase formation, and to experimentally evaluate and model these interphases in order to further elucidate their role in fiber-reinforced composites.

Surface modification by ^{60}Co gamma irradiation was used initially to graft acrylic polymers on the surface of ultra-high modulus (UHMPE) fibers. This technique utilized low dose rates and low total doses, and achieved grafting with retention of the exceptional UHMPE properties. The surface properties of the fibers were evaluated using fourier transform infra-red spectroscopy (FTIR), electron spectroscopy for chemical analysis (ESCA), and mechanical tests and dynamic mechanical spectrometry (DMS) of discontinuous fiber composites. Depending on the glass transition temperature, T_g , and chemical structure of the graft, the fiber/matrix adhesion and the interfacial failure mechanism

was tailored to provide either enhanced reinforcement or toughening. Using a three-phase block model, the DMS characteristics of the composites were modeled and the reinforcement efficiencies extrapolated as a function of surface treatment. The model successfully predicts the $\tan \delta$ response of the composite and the appearance of additional loss dispersions associated with the interphase. However, the interactions between the high-energy gamma radiation and the fiber and grafts yield interphases that are difficult to characterize and control.

The hydroperoxidation grafting method was subsequently developed, which permitted the grafting of tethered, linear chains by a free radical-type polymerization. Poly(styrene-*stat*-acrylonitrile) was grafted initially, in which the nitrogen in acrylonitrile was used as a marker to verify grafting and to estimate the grafting efficiency by ESCA analysis. Tapping mode™ atomic force microscopy (TMAFM) images of the grafted fibers revealed a nodular surface topography with dimensions that were correlated to the surface conformation of the grafts using a 'hard-sphere' model. Finally, three styrene/acrylonitrile/butyl acrylate interphases, each with a different copolymer composition, were grafted to evaluate the effect of interphase mechanics on the reinforcing and impact properties of woven-fiber-reinforced, three-phase composites. Accordingly, the interfacial and composite properties were tailored by varying the graft composition as well as the grafting efficiency. Moreover, the grafted interphases elicited a synergistic response in terms of the reinforcement and impact properties, a result previously unobtainable by oxidative-type surface treatments.

CHAPTER 1 INTRODUCTION

Polymer-Matrix Composites

Polymer-matrix composites (PMCs) represent a relatively new class of materials. Since their inception three decades ago, PMCs have become widely accepted and used and are now even recognized as a traditional material. Fiber-reinforced polymers are presently found in applications ranging from structural beams to railcar sidewalls, from helicopter rotor blades to golf club shafts, from musical instruments to tires, and from aircraft wings to lightweight, impact resistant automobile panels.

PMCs are generally comprised of two major constituents, the fiber reinforcement and the polymeric matrix material. The combination of these two yields a material with a unique set of properties, unachievable by either material separately. The fibers are considered the principal constituent since they constitute the largest volume fraction of material, and because the fibers support a major fraction of a load applied along the fiber direction. In unidirectional PMCs the ratio of the fiber and matrix moduli, $E_f/E_m > 10$. At volume fractions (v_f) of fiber exceeding 0.5, the fibers carry more than 90% of the load. Even at $v_f = 0.2$, a practical lower limit for most commercially available composite materials, the fibers support more than 70% of the applied load in a unidirectional composite. Since many fiber-reinforcement materials offer a combination of strength and

modulus that are either comparable to or better than traditional metallic materials, PMCs have emerged as a new high strength and high stiffness material.

Several of the commercially available high performance fibers are listed in Table 1-1. 1-3 A wide range of performance characteristics is possible through the selection of not only the type, but the volume fraction, orientation and fiber continuity (discontinuous short fiber or continuous fiber-reinforcement). The choice of fiber is dictated in large part by selection parameters such as specific gravity, strength, modulus, and elongation to failure, and of course, cost. For example, glass fibers represent a low cost, high tensile strength reinforcement with the disadvantages of a low tensile modulus and relatively high specific gravity. Carbon fibers provide an exceptionally high specific strength and modulus alternative with the main disadvantage of low impact resistance. The high performance polymeric fibers, Kevlar® (aramid) and Spectra® (polyethylene), are by far the most resistant to impact damage. Although their tensile stress-strain behavior is linear, fiber fracture of the polymeric fibers is usually preceded by longitudinal fragmentation, splintering, and even localized drawing. Such a non-catastrophic failure mode is not observed in carbon or glass fibers. Another outstanding feature of the polymeric fibers is their low specific gravity and correspondingly high specific properties. This aspect is particularly attractive for weight-sensitive applications, e.g., transportation, sporting goods, biomedical, etc. However, the oxidative susceptibility and low melting temperature (polyethylene) have limited the use of polymeric fibers to low-temperature applications and processing windows. Another significant drawback inherent to polymer-based fibers is their low surface energy relative to inorganic materials. This characteristic

Table 1-1. Typical Mechanical Properties Of High Performance Fibers

Fiber ^a	Strength (GPa)	Modulus (GPa)	Elongation (%)	Density (g/cm ³)	Specific Strength ^b (10 ³ m)	Specific Modulus ^b (10 ⁶ m)	Use Temperature (°C)
Spectra® 900	2.6	117	3.5	0.97	272	12.3	80-90
Spectra® 1000	3.0	172	2.7	0.97	315	18.1	80-90
Spectra® 1000 Plasma Treated	2.3	124	3.3	0.97	245	13	80-90
Kevlar 49 Aramid	2.8	124	2.8	1.44	198	8.8	160
Kevlar 149 Aramid	3.45	172	1.9	1.47	239	11.9	160
E-Glass	3.45	72	4.8	2.5	141	2.9	250
S-Glass	4.6	90	5.7	2.5	188	3.6	250
Thornel T-40 HS Graphite	5.65	290	1.8	1.81	312	160	>1500 ^c
Thornel P-120 HM Graphite	2.37	827	0.29	2.18	111	38.7	300

^aFiber Designation: Spectra® 900 (Allied-Signal Corporation, New Jersey, USA), Spectra® 1000 (Allied-Signal Corporation, New Jersey, USA), Spectra® 1000 - Plasma Treated (Allied-Signal Corporation, New Jersey, USA)

^b Specific Properties were computed by dividing the property value by the acceleration of gravity and the density. (units are meters)

^c Inert Atmosphere

is pivotal to acceptable processability and interfacial properties, both of which directly affect the overall composite performance.

The role of the matrix material in the composite is to maintain the alignment and placement of the fiber reinforcement as well as to protect the fibers from adverse environments and to transfer stresses between the fibers. In this regard, the matrix plays only a small role in the tensile load-carrying capacity of the composite. However, the matrix is integral to the mechanical performance of composites when a load is applied in a direction other than the fiber direction (off-axis). For example, the matrix provides lateral support and helps prevent fiber buckling under compressive loading. When a transverse tensile load is applied to the composite, the matrix properties are crucial since the fibers act as hard inclusions instead of load-carrying members. The local stresses and strains in the matrix surrounding the fibers are higher than the applied stress because of stress concentration. Near the fiber/matrix interface, the stress is tensile and nearly 50% higher than the applied tensile stress.³ Consequently, two types of failure predominate under transverse tensile loading, matrix cracking and fiber/matrix interfacial failure. Predicting and describing the composite response involves more than a superficial combination of fiber and matrix properties because of the complex nature of the fiber/matrix interface and its important role towards mechanical performance.

Fiber/Matrix Interfacial Properties

Mechanical properties of a composite depend not only on the properties of each primary component but also on the nature of the fiber surface, the extent of bonding between the fiber and matrix, and the mechanism of load transfer. Consequently, the

surface characteristics of the fiber and the chemical makeup of the matrix material control the interfacial properties. These aspects in turn affect the wettability of the fibers and the level of adhesion attainable at the fiber/matrix interface. Both are essential for effective stress transfer from the matrix to the fiber, and hence, optimum composite performance. Under ideal conditions, i.e., perfect adhesion between fiber and matrix, the composite properties, e.g., modulus, strength, density, coefficient of thermal expansion, etc., along the longitudinal direction of a unidirectional composite can be expressed according to the rule of mixture expression:

$$P_c = P_f v_f + P_m (1 - v_f)$$

By comparing the predicted property values with the measured values, the fiber reinforcement efficiency can be assessed. The reinforcement efficiency factors, K , of several unidirectional fiber-reinforced epoxy-matrix composites are graphically depicted in Figure 1-1. The reinforcement efficiency factor represents the ratio of the measured modulus, E_m , and the value predicted from the rule of mixture expression, E_c . K is a measure of the stress transfer capability of the fiber/matrix system. Hence, values of K can range from zero to one denoting conditions of poor and excellent stress transfer, respectively. Figure 1-1 shows that under tensile loading conditions where the load is applied parallel to the fibers the reinforcement efficiency is satisfactory for a majority of the high performance fibers. With the exception of the ultra-high modulus polyethylene (UHMPE) fibers, the values of K range from 0.8 to ca. 1.0. Although this result suggests that interfacial properties are quite satisfactory, at least for most of the high performance fibers, it does not give a complete picture.

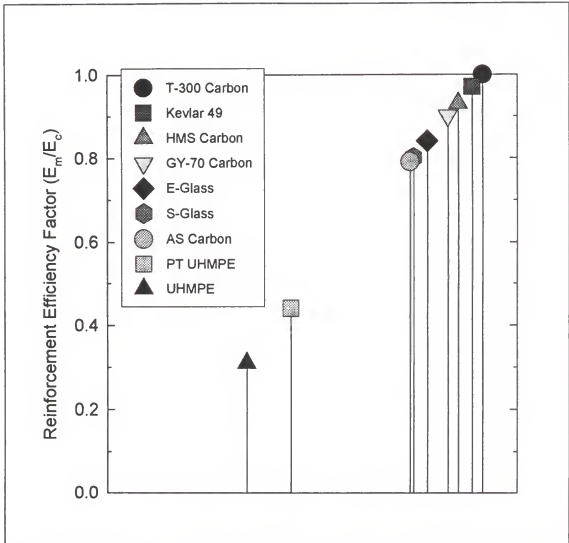


Figure 1-1. Reinforcement efficiency of selected high-performance-fiber/epoxy composites.^{1, 3}

A review of composite literature shows that most unidirectional composite materials incorporating high modulus fibers exhibit excellent performance along the fiber axis.⁴ However, loading conditions are not limited to simple, uni-axial loading geometries. Use of composite materials has expanded into structural applications for surface transportation, commercial aircraft and public works. The rigorous conditions to which these materials will be and are exposed require that they withstand complex stress conditions and yet maintain their competitive advantage of high specific strength and exhibit impact resistance. Both of these properties depend not only on the properties of each primary constituent but also on the nature of the fiber/matrix interface. Under tensile loading conditions in which the stress is oriented parallel to the fiber axis, increased fiber/matrix adhesion promotes better stress transfer from the matrix to fiber, providing better reinforcement efficiency. When off-axis stresses develop, the fiber/matrix adhesion plays an even greater role because of the shear stresses that are generated at the interface region. Table 1-2 lists the ranges of interlaminar shear strength (ILSS) values of some typical high performance fibers.⁵ In the case of carbon and glass fibers, these values are not quite as deficient as those for the high performance polymeric fibers, aramid and polyethylene. However, compared with the strength of the fibers themselves, the shear strength represents a weak link in the composite structure. Not surprisingly then, interfacial debonding is one of the most common types of failure observed in composite materials.⁶ If composites are to retain their competitive advantage as high strength, lightweight structures and find use in applications that are more demanding, then the fiber/matrix adhesion and corresponding off-axis properties must be significantly improved. Consequently, considerable effort has been focused on gaining a better

understanding of the interfacial region and elucidating its role in the performance of composite materials.

Table 1-2. Typical ILSS Ranges of High Performance Fibers.

<i>Fiber</i>	UHMPE	Aramid	Carbon	Glass
ILSS (MPa)	8-17	21-40	66-110	55-97

Interfaces and Interphases

Early on, it was assumed that the fiber/matrix interactions occurred over an infinitely thin region (zero thickness) and were governed solely by the fiber surface and matrix molecular chemistry. Thus, the area over which these interactions occurred was referred to as the *interface*. The level of adhesion in early composites was also considered secondary because of the limited selection of materials and the acceptance of “satisfactory” performance. As the pool of candidate materials expanded through the advent of new polymeric matrices and new higher performance reinforcing fibers, consideration of these materials for more demanding, technologically significant applications also evolved. No longer was the level of adhesion satisfactory with the ever-increasing performance demands. This led to the need for a more fundamental understanding and investigation of the mechanisms of adhesion between fiber and matrix and its effect on composite properties.⁷

Several investigators have since substantiated the existence of a thin but distinct interphase between the fiber and matrix.^{7, 8} The concept of a two-dimensional interface has given way to the three-dimensional region more properly termed an interphase. The *interphase* forms a region around the fiber with a finite thickness and properties distinct

from the bulk of the matrix. The different properties may be a result of local variations of the matrix microstructure in proximity to the fiber surface, radial variations in the fiber morphology and chemical composition, and/or impurities, voids, adsorbed species, unreacted monomers, matrix additives, etc. Imposed upon the interphase are the processing conditions that permit chemical reactions, volumetric changes and residual stresses to form.⁷ In short, the interphase represents a very complex region that merits further investigation because of its impact on composite performance and behavior.

One of the areas with the greatest technological potential is the concept of three-phase composites. Three-phase composites are made by purposefully engineering an interphase region between the fiber and matrix. Traditionally, there has been a trade-off between the optimization of stress transfer and energy dissipation mechanisms. When surface treatments are used to improve fiber/matrix adhesion, there is generally a loss in impact resistance because of the higher interfacial shear strength. Tailored interphases provide the composite engineer with the opportunity to design interphase regions that (i) improve wettability and hence, processability, (ii) promote stress transfer through fiber/interphase/matrix interactions and adhesion, and (iii) provide greater energy absorption through novel interfacial failure processes. The research reported in this dissertation is part of an effort to investigate, characterize and design interphases in order to provide the underpinnings for a predictive description of fiber/matrix adhesion and its relation to composite performance.

Experimental Summary

As shown above, UHMPE fibers exhibit outstanding specific strength and modulus exceeding those of nearly all other commercially available fibers (Table 1-1). In addition, their excellent chemical, fatigue and abrasion resistance make them an attractive candidate for reinforcement of low temperature, high performance composites used in, e.g., biomedical devices, low-mass, high-performance automobile parts, sporting goods and antiballistic applications. However, the use of these high performance fibers has been limited largely by their poor adhesion characteristics. This aspect has served as the impetus for continuing efforts towards the surface modification of UHMPE fibers. Unfortunately, many of the strategies employed toward the goal of improving surface properties have done so at the expense of other equally important properties such as fiber mechanical properties (strength and modulus) and impact resistance. This work focuses on surface modification techniques that allow us to design an interphase region and tailor the overall composite response without loss of fiber properties or composite impact performance. In particular, the surface properties of UHMPE fibers are studied and modification routes for composite interphase design are rigorously evaluated.

This study consists of three-parts. The first part, chapters 3 and 4, describes our initial efforts to develop a technique for surface modification by gamma radiation induced grafting. A set of acrylic polymers are grafted, one with a very low T_g (rubbery at room temperature) and a polymer with a high T_g (glassy at room temperature), and evaluated. Depending on the glass transition temperature (T_g) and chemical structure of the polymer grafts, the interphase properties may be tailored to provide significantly improved

reinforcement or toughened composites (chapter 3). This was accomplished without sacrificing fiber mechanical properties. In chapter 4, the dynamic mechanical properties of thermoplastic-matrix, discontinuous-UHMPE-fiber-reinforced composites are evaluated and deconvoluted using a three-phase block model. This analysis is especially advantageous since the fiber-reinforcement efficiency factor can be extracted from the model for a range of interfacial conditions.

One of the consequences of using UHMPE fibers is the limited temperature range over which these fibers may be processed and used. Processing at temperatures as low as 100°C can induce melting and recrystallization of the fibers. Hence, the second part (chapter 5) of this work elucidates the effect of annealing temperature on the bulk crystalline content and structure, surface morphology and tensile properties. Armed with a better understanding about the unique morphology of UHMPE fibers, it is possible to design edifying experiments around the topic of interphase development.

Although it is possible to design interphases using gamma radiation surface grafting, this technique is not free of limitations. The very nature of the grafting process, i.e., grafting through interaction of the PE molecules with high-energy gamma radiation, leads to the formation of highly crosslinked interphase polymers, or “hyper-branching.” This adverse feature manifests itself in the lack of control afforded during the graft polymerization process because of the complex initiation mechanism. Hence, a grafting method is sought that provides a method of designing and synthesizing well-controlled interphases. Chapter 6 describes a novel grafting method based on hydroperoxidation of the UHMPE fiber surface and subsequent free radical initiated grafting. This technique permits the design of polymeric interphases with tunable properties. Based on a shear lag

theoretical approach, the interphase is then engineered by adjusting the chemical composition, and hence T_g and modulus, in order to tailor the composite response (chapter 7).

CHAPTER 2 BACKGROUND

According to the Advanced Materials Agenda submitted in 1993 to the Presidential Administration and the 103rd Congress by the Suppliers of Advanced Composites Materials Association, several expanding markets for polymer matrix composites exist. These include the following: (i) surface transportation, (ii) commercial aircraft, (iii) public works, (iv) marine structures, (v) oil exploration and (vi) energy storage and conversion.⁹ Polymer matrix composites, in particular, are being considered because they offer many advantages over traditional materials. Their low density provides very high specific strength and stiffness which, e.g., will improve energy efficiency and lessen the environmental impact in the transportation industry. Furthermore, costs are reduced by parts consolidation, and corrosion resistance is improved considerably over welded steel components. One potential hindrance to the use of fiber-reinforced, polymer-matrix composites is their highly anisotropic nature. This feature is very favorable for stresses oriented along the fiber axis. However, an inherent deficiency of PMCs is their generally poor performance under an applied off-axis stress. The off-axis properties are critical if composites are to retain their competitive advantage as high strength, lightweight structures and find use in more of the demanding applications such as those listed above. The off-axis properties are strongly dependent on the fiber/matrix adhesion and the corresponding transfer of stress through the interface or interphase. Likewise, the fracture toughness and impact resistance of composites depends on energy dissipation via

fiber/matrix debonding, fiber pullout, and other interfacial failure mechanisms. Both the adhesion, and hence reinforcement, and damage tolerance-related properties of PMCs are integral to their selection and success in more rigorous applications. However, the lack of mutual exclusivity between these two material properties has led to two separate strategies for improvements in these areas. Generally, surface treatments that improve fiber/matrix adhesion do so at the expense of impact performance. Conversely, the current methods for improving impact properties typically rely on designs that promote interfacial weakening and failure. This section will review the common methods employed to improve either adhesion or impact performance in composites, and will highlight the critical needs in the area of surface modification for future composite materials, in particular UHMPE fiber reinforced composites.

UHMPE fibers are particularly attractive as a reinforcement material in light of the critical needs addressed above. Its mechanical properties compare favorably with other reinforcement materials and with a density of 0.97 g/cm^3 , the specific properties exceed most fibers with the exception of high-strength carbon, to which it is comparable. However, the poor adhesion characteristics of UHMPE fibers have limited its application. For these reasons UHMPE fibers are recognized as an excellent opportunity to develop novel surface modification techniques and further advance their utilization and composite performance overall. The following sections will therefore address various surface modification techniques as they relate to fiber/matrix adhesion and impact performance, and will in particular summarize the most recent trends in the surface modification of the high performance UHMPE fibers.

Fiber/matrix Adhesion

Effective reinforcement for strength and modulus by any fiber requires good stress transfer. Adequate fiber/matrix adhesion then is a prerequisite for satisfactory strength and modulus. Although fiber/matrix adhesion is critical to the mechanical properties of fiber reinforced composites, the science of adhesion is still a complex phenomenon for which no universal theory exists. This is mainly because adhesion embraces a large number of notions and concepts that can vary, depending on whether the phenomenon is observed at a molecular or at a macroscopic level.¹⁰ In polymer matrix composites, three types of interactions between the constituents, on both the macroscopic and microscopic levels, constitute fiber/matrix adhesion. These are (i) mechanical interlocking, (ii) chemical bonding and (iii) physicochemical bonding.

Mechanical interlocking occurs when one species infiltrates into the pores or surface roughness of the other, or when two rough surfaces are intermeshed. Since pore sizes generally fall in the micron size range, this type of bonding is considered a form of macroscopic adhesion that can nonetheless lead to high levels of interfacial strength. Rigorous plasma treatments of UHMPE fibers, for example, cause extensive macro-scale surface etching and pitting that lead to fiber/matrix mechanical interlocking and improved adhesion.^{1, 2, 11} However, this type of surface modification can also be deleterious to the fiber mechanical properties because of the introduction of defects along the surface of notch-sensitive fibers. With the growing interest in interphase properties, grafting has emerged as another method of promoting fiber-surface/matrix mechanical interlocking, yet on a molecular scale. If the grafts and/or matrix molecules exhibit mutual solubility and

high individual diffusivities, interdiffusion can occur leading to the formation of molecular-scale interlocking, or entanglements. This is analogous to the mixing of polymers, in which the strength of the interphase between the two incompatible materials is controlled by the extent of chain coupling. Thus, if the graft is chemically attached to the fiber and mixes well with the matrix a considerable improvement in adhesion can be realized. This approach is frequently employed to improve compatibility between immiscible polymers using random or block copolymers.¹² It is also recognized as a method of improving fracture toughness of polymer blends through selected interfacial failure mechanisms.¹³

The second type of interaction between the fiber and matrix is chemical bonding. Numerous surface modification routes exist that functionalize the surface with reactive sites for chemical bonding. Some of the reactive moieties include amine, carboxylic acid, hydroxyl and other chemical species that are capable of reacting with the matrix to form either covalent, ionic or metallic bonds. Although chemical covalent bonds occur over a very small distance and involve few molecules relative to other types of interactions, the bond energies (60 to 700 kJ/mol) are significantly higher in magnitude than those for physical bonding (2 to 40 kJ/mol). Consequently, adhesion by chemical bonding is comparatively strong. For example, Gao and Zeng determined the contribution of chemical bonding relative to other mechanisms of adhesion for plasma treated UHMPE fibers.¹⁴ Its contribution to adhesion comprised 61% of the total in contrast to mechanical interlocking and physicochemical bonding whose individual contributions equaled 26% and 13%, respectively.

While physicochemical bonding generally represents a small fraction of the overall adhesive strength, this mode of interaction should not be overlooked. Physicochemical

interactions may develop because of mismatches in the coefficients of thermal expansion, polymerization shrinkage, and/or other volumetric effects. Physicochemical bonding is also strongly influenced by the surface energy of both the fiber and matrix. Wetting is related, thermodynamically, to the difference in surface energies of the constituents and thorough wetting is a fundamental requirement for high levels of adhesion. Thus, treatments that increase the surface free energy of the fiber improve physicochemical bonding. Physical bonding may also be represented by van der Waals forces, H-bonding, polar-polar bonds, etc. Thus, treatments that cause surface roughening increase the fiber/matrix interaction area and increase the overall magnitude of physical bonding.

Therefore, the quality of adhesion is related to the surface characteristics of the fiber in terms of the (i) surface morphology, topography and roughness, (ii) surface energetics and wettability and (iii) chemical functionality; and the contribution of each to the level of adhesion is additive.¹¹ Thus, surface treatment schemes that enhance any of these characteristics for UHMPE fibers, as well as other high performance fibers, will improve their reinforcement efficiency in composites.

Characterization of Interfacial Properties

The level of fiber/matrix adhesion for a fiber/matrix system is typically characterized using either a simple fiber pullout test, the microbond technique, or by measuring the interlaminar shear strength (ILSS) using the short beam shear test. The pullout experiment consists of a single fiber embedded in a block or disc of resin. A steadily increasing force is then applied until the interfacial shear strength (IFSS) is exceeded and fiber pullout commences. The microbond technique utilizes very small spherical or elliptical droplets of resin through which the fiber is pulled free. The average

IFSS is calculated by dividing the maximum measured force of debonding by the area of the embedded fiber length. Although both of these techniques allow characterization of a variety of fiber/matrix combinations, they are limited by their sensitivity to measurement conditions. Differences in embedded fiber length, microdrop size, location of contact points on the droplet, meniscus effects, gripping pressure and other variations in conditions cause large scatter in the data. Herrera-Franco and Drzal have compared the single-fiber methods with the composite properties obtained from, e.g., the short beam shear test. The short beam shear test (ASTM D-2344) utilizes a three-point flexure geometry with a span-to-depth ratio chosen so as to maximize the out-of-plane shear stress relative to the tensile stress and produce interlaminar shear failure of an actual composite sample. The interlaminar shear strength (ILSS) is written in terms of the failure load, P , and the cross sectional area, A as

Herrera-Franco and Drzal concluded that the single-fiber tests do not offer a complete and

$$ILSS = 1.5 \times \frac{P/2}{A}$$

unambiguous method for measuring the interfacial shear strength between fiber and matrix.¹⁵ However, the single-fiber tests produce values of interfacial shear strength that are, at least according to trend, similar to other composite-based testing methods. Table 2-1 lists the values of interfacial shear strength using these three methods for UHMPE fibers with a variety of surface treatments. Within each test method, a considerable amount of variability is observed even though the fiber type, Spectra® (Spectra® is a trademark of UHMPE fibers, Allied Signal, Inc.), is essentially the same for each.

Table 2-1. Summary of UHMPE Surface Treatments and Interfacial Strengths.

Treatment (atmosphere)	Spectra® PE Fibers	Method	Shear Strength (MPa)		Tensile Strength (GPa)		Ref.
			Untreated	Treated	Untreated	Treated	
plasma (O ₂)	1000	ILSS	7.2	22.0	2.6	2.3	16
plasma (NH ₃)	1000	ILSS			NA	NA	17
1 minute			5.7	11.1			
2 minutes				11.8			
10 minutes				11.8			
silane treated	900	ILSS	10.8	14.3	NA	NA	18
plasma (O ₂)			10.8	25.4			
plasma (O ₂) + silane			10.8	28.4			
plasma (O ₂)	1000 ^a	ILSS	3.2	6.9	NA	NA	19
plasma (NH ₃)	1000 ^a	ILSS	3.2	6.4	NA	NA	19
plasma ^b	900 ^a	ILSS	6	15	2.6	2.3	1
corona	1000	ILSS	5.7	7.0	NA	NA	17
corona	900 ^a	ILSS	6	10	2.6	2.5	1
corona	1000 ^a	ILSS	3.2	5.4	NA	NA	19
acid (nitric- 85°C)	900	ILSS	9.5	14.5	NA	NA	21
plasma (Ar)	900	pullout	0.85	1.60	2.25	1.26	20
plasma (Ar + allylamine)	900	pullout	0.85	4.03	2.2	2.25	20
plasma (CO ₂)	900	pullout	0.62	1.50	3.4	3.1	23
	1000		0.81	1.55	3.6	3.4	
plasma (N ₂)	900	pullout	0.62	1.66	3.4	3.5	23
	1000		0.81	1.80	3.6	4.3	
plasma (allylamine)	900	pullout	0.56	1.73	NA	NA	5
acid	900	pullout	1.81	2.67	2.3	2.1	24
(1HCl:1Nitric)	1000		1.75	2.63	3.1	2.9	
UV	900	pullout	0.3	0.8	2.6	2.7	25
(acrylic acid)							
UV	900	pullout	0.3	1.3	2.6	2.5	25
(acrylamide)							
acid (K ₂ Cr ₂ O ₇)	1000	MB	1.7	11.3	3.2 ^c	2.4 ^c	26
acid (KMnO ₄)	1000	MB	1.7	3.2	3.2 ^c	2.9 ^c	26
acid (H ₂ O ₂)	1000	MB	1.7	1.3	3.2 ^c	2.4 ^c	26

^aILSS results obtained from 0/90, plain-weave composites; ^bPlasma carrier gas deemed proprietary by Allied Signal, Inc.; ^cTensile properties taken from ref. 27; Abbreviations: NA, not available; ILSS, interlaminar shear strength; MB, microbond test; UV, ultraviolet radiation

Likewise, there is a considerable difference in shear strength values across each test method. These differences are partially attributable to the differences in matrix material and processing conditions for each. Therefore, conclusions about different surface treatments should be based upon both a review of each surface treatment procedure and the choice of testing methods.

Surface Modification of UHMPE Fibers

A variety of surface treatments exist for the modification of UHMPE fibers, utilizing for instance, radio frequency (rf) plasma, chemical and UV-radiation, gamma and E-beam radiation sources. Brennan²⁸ and George²⁹ have each compiled a comprehensive review outlining these techniques. Surface treatments by plasma exposure are the most common medium by which the PE fibers have been modified for improved adhesion. Surface modification by plasma involves a complex series of reactions with a small amount of ions (ppm), a small percent of free radicals (2-20%), and the remainder comprising extremely energetic UV radiation created by the excitation of a gas at either a reduced pressure or ambient pressure.³⁰ The interaction between plasma and the surface can be classified in general terms as either polymer-forming or non-polymer-forming (ablative plasma). The latter process may include surface cleaning, micro-etching, crosslinking and/or surface activation. While these effects are potentially advantageous in terms of enhanced adhesion, the ablation process can actually reduce the fiber mechanical properties. The polymer-forming plasma is attractive since the organic species that is polymerized can be chosen to yield a highly functionalized surface.

Plasma surface modification

In one of the earliest studies of plasma treatment of melt-spun polyethylene fibers, Ladizesky and Ward showed that an oxygen gas-plasma treatment improved the interfacial shear strength (IFSS) ten-fold over untreated fibers.³¹ Scanning electron microscopy showed that the plasma etches the surface causing extensive pitting. Thus, the enhancement in adhesion as determined by a fiber pullout test was attributed to mechanical interlocks between fiber and matrix. These fibers also exhibited an approximate 50% decrease in the fiber tensile strength related to the formation of surface defects following extensive etching of the fiber surface. In addition, the authors also concluded from pullout tests that the fibers failed cohesively rather than interfacially following the plasma treatment.

Nardin and Ward subsequently set out to elucidate the mechanisms of adhesion as they pertained to plasma surface modification.¹¹ They mathematically determined the contributions of each of the three components of adhesion: (i) chemical bonding, (ii) mechanical interlocking and (iii) physicochemical bonding, and showed that the contribution from each towards the overall adhesion was additive. Moreover, they derived empirical relationships between the degree of physicochemical bonding and the fiber surface energy, and the extent of mechanical interlocking and the depth of surface pits. The physicochemical bonding is directly proportional to the surface energy of the fibers, and the fiber pullout stress increases linearly with pit depth. The latter phenomenon can be explained by the increased surface area over which greater extents of mechanical interlocking and physicochemical bonding can occur. However, there is a decrease in

tensile strength corresponding with a higher surface area and the generation of surface defects.

Following the development of the gel-spinning process, Allied Signal, Inc. implemented a commercial plasma treatment of Spectra® 900 and 1000 (UHMPE) fibers to improve their adhesion properties. The high-strength and modulus polyethylene (PE) fibers are manufactured by a gel-spinning process in which an ultrahigh molar mass ($M_w=1.5 \times 10^6$ g/mol) PE is extruded through a small diameter spinneret and subsequently drawn at elevated temperatures. This process induces the highly oriented and crystalline structure and yields a fiber with exceptional strength and stiffness. The proprietary gas plasma treatment (presumably oxygen based on FTIR and ESCA analysis results) improves the flexural strength and modulus by 60% and 40%, respectively.³¹ Likewise, the ILSS of plasma treated Spectra® 900 and 1000 composites increase by a factor of 2.9 and 1.4, respectively, but the fiber tensile strength decreases by 10% following the treatment (Table 2-1).^{1, 32}

Other studies followed in an attempt to optimize the plasma treatment parameters by varying treatment time, power, pressure, and type of gas. In particular, amination of Spectra® PE fibers by ammonia plasma was achieved with similar improvements in the surface characteristics, i.e., increase in surface energy and wettability.^{34, 35} In this case, the tensile strength and modulus of single filaments decreased by 10% under conditions that optimized amine concentration, and hence wettability and chemical functionality. In a related study, Brown *et al.* demonstrated that an ammonia plasma treatment results in improvements in the ILSS, fracture energy, and flexural modulus and strength of

Spectra[®]-fabric-reinforced epoxy composites.¹⁷ These improvements are related to the introduction of surface amine groups that provide chemical bonding sites with the epoxy matrix. While the concentration of amine groups increases monotonically with treatment time, the ILSS and interlaminar fracture energy are optimized at a treatment time of two minutes. However, the V_{50} ballistic limit (projectile velocity at which the probability of target penetration is 50%) of Spectra[®] reinforced epoxy composites decreases with increasing plasma treatment time. This important result is consistent with the observation that composite impact performance is enhanced by a reduction in interfacial properties.

In an extension of this work, Brown *et al.* compared the efficacy of oxygen plasma and ammonia plasma-treated UHMPE fibers in a vinyl ester resin. As shown in Table 2-1, the oxygen plasma yields a slight improvement in the ILSS value relative to the ammonia plasma treatment, yet the improvements in flexural properties are comparable.¹⁹ Although the authors contend that chemical bonding occurs between neither the oxygen nor the ammonia-plasma treated fibers and the vinyl ester resin, it is not possible to thoroughly explain the differences between plasma-gases since a complete analysis of surface properties in terms of the surface energy, concentration of oxidative species and surface morphology was not given.

The utility of plasma treatments for the enhancement of adhesion mechanisms was further explored by Hild and Schwartz.^{23, 36} In this study, the effect of gas-type was evaluated using nitrogen, argon, and carbon dioxide for various treatment times. Deconvoluted C1s spectra from ESCA analysis show that the surface is comprised of oxidative species following each of the gas-plasma treatments. Thus, the increased IFSS (Table 2-1) is attributed to improved wettability and physicochemical bonding related to

the addition of polar groups along the surface. The authors conjecture that during the plasma treatment, regardless of the gas-type, free radicals form on the fiber surface which, upon exposure to air, become oxidized.³⁶ This aspect of plasma surface modification is important for polymer-forming treatments. Although the authors cited no changes in surface topography up to a magnification of 2000X, the SEM images reveal distinct surface cracking along the length of the fiber. They attribute this to handling during the pullout testing.

The interpretation of morphological changes using SEM is open to misinterpretation. There is not a standard method of preparation nor are there standard SEM operating conditions for polymeric fibers. Consequently, surface damage is possible either during plasma coating as well as when the fiber is exposed to the electron beam of the SEM. Figure 2-1 illustrates the surface artifacts that can be induced by improper conditions of sample coating of a commercially available plasma-treated (PT) Spectra® 1000 fiber.²⁸ The first SEM micrograph, Fig. 2-1a, shows the surface of the fiber after plasma coating with Au-Pd at 9 kV and 30 seconds. The smooth surface topography of these fibers is evident and characterized by the longitudinal striations that are a consequence of the extrusion and drawing processing operations. The bottom figure, Fig. 2-1b, represents a fiber from the same fiber bundle as the sample in Fig. 2-1a, except that it is coated with Au-Pd at 9 kV of power for 180 seconds. There is extensive damage caused by the longer exposure to the plasma during the coating process. Unfortunately, this could be misconstrued as surface etching from the initial plasma treatment. Care should be taken to define sample preparation conditions that prevent surface damage and analysis parameters should be set that prevent beam damage. One possibility is to view

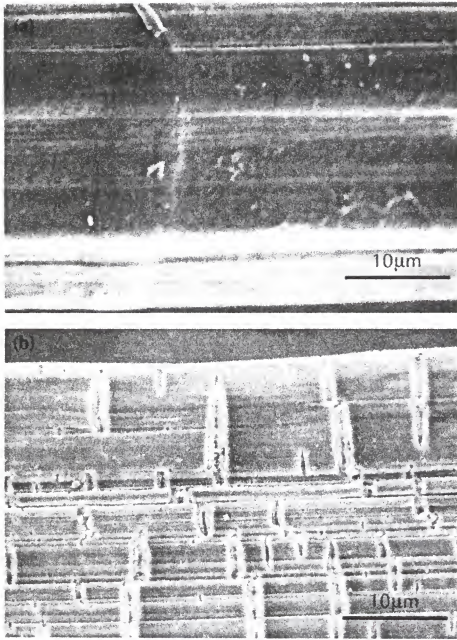


Figure 2-1. SEM micrographs of (a) PT Spectra[®] 1000 {conditions: 5 keV, magnification x 1700, Au-Pd coating (9 kV, 30s, 13 Pa)} and (b) PT Spectra[®] 1000 {conditions: 5 keV, magnification x 1700, Au-Pd coating (9 kV, 180s, 13 Pa)} highlighting the damage that can be caused by excessive coating time.²⁸

the samples at low voltages so that the samples can be imaged directly after the surface modification step, which would eliminate any surface damage caused by sample preparation and/or electron-beam exposure.³⁷

The effect of oxygen plasma treatment on commercially available UHMPE fibers was further evaluated by Woods and Ward.¹⁶ Upon exposing Spectra® PE fibers to oxygen-gas plasma, the ILSS increases nearly three-fold (Table 2-1). This improvement was attributed to several effects. First, and most dominant in terms of adhesion, the surface is oxidized within seconds of initial exposure.¹⁶ As described by Hild and Schwartz, the surface functionalization increases wettability and promotes both chemical and physicochemical bonding with the epoxy matrix.³⁶ Second, the oxygen plasma produces a pattern of micro-pits on the surface, forming sites for mechanical interlocking with the matrix. The third effect of plasma treatment was attributed to the existence of low molar mass impurities presiding at the fiber surface. These species are believed to form a weak boundary layer (WBL) at the surface. Upon plasma exposure, it is postulated that this weak layer is crosslinked and subsequently strengthened. However, the presence of oxygen acts as radical scavengers thus promoting chain scission rather than crosslinking. A comparison of oxygen and nitrogen-gas plasma treatments shows that crosslinking occurs more rapidly and to greater extents in the nitrogen atmosphere. An incubation period for crosslinking is observed for oxygen atmospheres, presumably, according to the authors, because of oxygen consumption at the outer surface layer.¹⁶ Another important observation made was the apparent maximum ILSS attainable prior to a significant decrease in the fiber tensile strength. After extensive plasma treatments,

severe etching of the fiber surface occurs and the fiber tensile strength drops precipitously.

In addition to crosslinking, the deleterious effects of the WBL can be remedied by removing the outer surface layer. Rostami *et al.* used argon plasma followed by reaction with allylamine to increase the IFSS of Spectra® 900 fibers.²⁰ After treating the fibers with only the argon plasma, Rostami *et al.* showed that the diameter of single fibers was severely reduced. This contrasted with most of the previous work where fiber bundles were treated and the change in diameter of a single fiber was not considered. It also revealed that the both the fiber diameter and tensile strength decreased considerably after relatively short exposure times. For example, the diameter and tensile strength dropped 19% each following a 15 second treatment.²⁰ The IFSS increased with ablation of the fiber surface because of the removal of the WBL and the roughening of the fiber surface. When the plasma treatment was continued to the point that the surface became smooth again, there was a concomitant decrease in the IFSS value because of the lack of mechanical interlocking. If the fibers were treated with the argon plasma followed by an allylamine plasma treatment, the surface was grafted. This effect is advantageous since the adverse effect of plasma etching is mitigated through surface regeneration. The ramifications of this approach are that the diameter is not changed at short exposure times, and at longer times some growth is actually experienced. Consequently, the tensile strength is retained and the IFSS is dramatically improved, four-fold for the optimum argon/allylamine combination treatment.

The effect of chemical treatments on UHMPE fiber adhesion has not received the same level of attention as plasma. Nonetheless, the adhesion and wetting characteristics of UHMPE fibers can be improved using nitric acid, chromic acid, chlorosulfonic acid and

other oxidants to modify the surface characteristics. For example, Taboudoucht *et al.* reported an increase in the ILSS but cited only minimal improvements in the flexural strength and modulus of nitric-acid-treated-UHMPE-fiber/epoxy composites.²¹ Ulcay *et al.* showed that chemical treatments with a 50:50 hydrochloric acid/nitric acid solution improve interfacial bonding determined by pullout tests, but lowers the tensile strength of the individual fibers.²⁴ Similarly, Silverstein showed that different oxidants could be used to remove the WBL, etch the surface and significantly improve the fiber/matrix adhesion.^{26, 27} Chromic acid, potassium permanganate and hydrogen peroxide were compared. Chromic acid, the more powerful oxidant, caused noticeable surface etching, resulting in a six-fold improvement in the IFSS, as determined by the microbond technique.^{26, 27} However, the optimum soak time for chromic acid also leads to a 25% reduction in fiber tensile strength. The wet chemical approach is analogous to gas-plasma surface modification in that the surface is altered by oxidation and etching.

The efficacy of gas-plasma surface modification is obviously a function of the carrier gas, gas purity, and experimental conditions such as power of the rf generator, pressure and time of exposure. Its measured effect on the adhesive properties of UHMPE fibers is also dependent on the characterization method, testing conditions, fiber type, matrix material, and curing profile. Nevertheless, the preponderance of literature indicates that non-polymer-forming plasma effectively improves the adhesion properties of UHMPE fibers. However, there are inherent drawbacks to this approach. Mainly, the plasma treatments, and chemical treatments for that matter, described thus far are ablative in nature. Although this feature helps to remove the weak boundary layer, if present, and

enhance adhesion through mechanical interlocking, severe and extensive surface damage is deleterious to the fiber mechanical properties. It is a general rule that greater interfacial shear strength is exchanged for lower tensile strengths following plasma treatment.

Considering that many of the high performance fibers are already cost prohibitive, this aspect of surface modification represents a serious downside. It is also clear that plasma treatment is an effective method to functionalize polymeric surfaces thereby increasing the surface energy and promoting chemical and physicochemical bonding between the fiber and matrix. However, this surface-only approach is also deficient since the modified surface is not always stable over time.

Gao and Zeng have demonstrated the effect of aging at ambient conditions on the surface free energy of ultra-high molar mass fibers treated with an oxygen plasma.¹⁴ After ten days the surface free energy had decreased by more than 10%, which was attributed to molecular rearrangement by thermally activated motions. Similarly, Volpe *et al.* showed that the reduction in the advancing contact angle following air-plasma treatment is unstable at ambient conditions.²² After 10 days the value increases by ca. 25% and at the conclusion of another 180 days of aging the value increases an additional 20%. As expected, this effect is exacerbated by an increase in temperature. After only two hours at 90°C, the advancing contact angle of air-plasma treated UHMPE fibers increases by 33%.²² The stability of the plasma treatment following the incorporation of the UHMPE fibers into an epoxy matrix was also quantified using the pullout method. Only a minor decrease (3%) in the IFSS was observed after aging the composite samples 25 days.²² The authors hypothesized that the matrix molecules bind the fiber surface

species, either chemically or physicochemically, thus inhibiting any considerable molecular rearrangement during composite processing, curing and/or storage.²² Choe and Jang recognized this deficiency of plasma surface modification and attempted to stabilize the surface using various silane coupling agents.¹⁸ Following an oxygen-gas-plasma treatment, Spectra® 900 fibers were immersed in one of the silanes: (i) γ -methacryloxypropyltrimethoxy silane (MPS), (ii) vinyltriacetoxysilane (VTS), (iii) γ -aminopropyltriethoxy silane (APS) (iv) 3-(N-styryl-methyl-2-amino-ethylamino) propyltrimethoxy silane hydrochloride (SAPS). Although the effect on surface stability was not clearly reported in the paper, the combination of plasma and silane (SAPS) treatments resulted in a 160% improvement in the ILSS (epoxy matrix) relative to the untreated fibers.¹⁸ This ILSS value represented a 100% improvement over the silane-only treatment and a 12% improvement over the plasma-only. When the effect of this treatment was evaluated in a vinyl ester matrix, the SAPS and MPS silanes, surprisingly, were the only two that yielded an improvement in the ILSS relative to the plasma-only treatment. Another important observation was that an optimum silane concentration exists for surface modification following the plasma exposure. For the most effective silane in the vinyl ester matrix, MPS, the optimum silane concentration is 0.3 weight percent.¹⁸ This most likely reflects an ideal surface structure in terms of packing geometry, multi-layered structure and accessibility of the vinyl functionality of the MPS.

The disadvantages of conventional plasma treatments of UHMPE fibers have led to the development of several grafting techniques. The premise behind this approach is that surface grafting can be used to impart the desired surface response while retaining the

bulk properties of the substrate polymer. Generally, a monomer is chosen that will increase the fiber surface energy and enhance wettability, and/or a monomer with reactive pendant groups that provides a chemical bond with the matrix material is selected. As noted above, there are multitudes of oxidative, non-grafting treatments that improve wettability. Some even provides reactive functionality for chemical bonding. However, polymer grafting represents a novel method to “hyper” treat the surface and exponentially increase the number of desired functionalities through the graft polymerization process. The anticipated advantages of this approach include enhanced surface stability, the mitigation of the WBL, and retained fiber properties because of the surface crosslinking and growth processes inherent to the polymer-forming plasma method.

Table 2-2 provides a list of the various monomers grafted to UHMPE fibers by the different methods. The most widely used grafting method is rf plasma exposure in which two routes of grafting are viable. The first permits grafting by introducing monomer during the plasma treatment. Li and Netravali employed an allylamine plasma to graft onto the surface of Spectra® 900 fibers.³⁸ This choice of monomers provides high levels of crosslinking and yields primary amines along the surface with which the matrix can chemically bond. While the presence of amine functionalities was only indirectly confirmed by analysis of the graft on a glass slide, the IFSS (pullout) showed an increase by a factor of two to three for plasma-treated fibers over untreated UHMPE fibers.^{5, 38} Although the fiber tensile strength was not significantly affected by the plasma time, the overall strength decreased monotonically with the power level.⁵ The fact that this result contradicts the findings of Rostami *et al.* further confirms the conclusion that the

effectiveness of any plasma treatment depends on the pre-treatment conditions and the specific plasma parameters.

Table 2-2. Summary of UHMPE Fiber Surface Grafting Methods and Monomers.

PLASMA	GAMMA	UV-RADIATION	E-BEAM
Acrylamide (Peroxide) ³⁹	Acrylic Acid-HDPE Fibers ⁴⁰	Acrylamide 25	Acrylic Acid ⁴¹
Glycidyl Methacrylate (Peroxide) ³⁹	Butyl Acrylate ³³	Acrylic Acid 25	
Allylamine ⁵	Cyclohexyl Methacrylate ³³		
Ethylene (Ziegler- Natta) ⁴²	Methyl Methacrylate n-Vinyl Pyrrolidone Allyl Alcohol ⁴³		

The second plasma-grafting method utilizes non-polymer-forming gases in the plasma chamber that yield reactive chemical moieties on the fiber surface. These are subsequently used to initiate grafting off the surface. For example, Mori *et al.* used an argon-plasma pre-treatment followed by exposure to air to introduce peroxide groups onto the surface of UHMPE fibers.³⁹ Graft polymerization of acrylamide (AAm) and glycidyl methacrylate (GMA) was subsequently performed in either deaerated monomer solution at elevated temperatures, or in aerated monomer solution under UV radiation. Although neither the fiber mechanical properties nor the fiber/matrix adhesion properties were characterized, FTIR and ESCA analysis confirm the presence of AAm and GMA grafts. As expected, the combination of peroxide and UV radiation initiation mechanisms yields higher grafting rates than the peroxidation-only method.³⁹ Similarly, Wang *et al.*

used an oxygen-gas plasma treatment on Spectra® 900 fibers to prepare the surface for attachment of Ziegler-Natta type catalysts. The surface was subsequently grafted with considerable quantities of polyethylene. When these fibers are incorporated in a polyethylene matrix, the modulus, strength and elongation to failure increase for PE filled with the grafted fibers compared with ungrafted plasma-treated fibers.⁴² Although neither of these methods was used strictly to design an interphase, they demonstrate two feasible approaches to creating an interphase with well-controlled and tailored properties. Unlike the first plasma grafting method, these examples illustrate the possibility of linear, non-crosslinked interphases where a better understanding of the role of the interphase region might be grasped.

Radiation-induced grafting

Radiation processes such as UV and gamma radiation are also used extensively for surface grafting. The main differences between the effects of the UV radiation generated in a plasma reactor and gamma radiation are their depth of penetration. The influence of UV radiation is limited to the upper few hundred angstroms of the surface whereas the very high-energy gamma radiation penetrates into the bulk of the material. Both techniques, however, generate cations, cation radicals, free radicals and other reactive intermediates that lead to complex grafting mechanisms. The first published data on grafting onto polyethylene fibers was disclosed by Kaji *et al.*⁴⁰ These fibers were made of high-density polyethylene and were modified using acrylic acid. By converting the acrylic acid grafts to their metallic salts through the addition of cations such as Li, Na, K and Mg, the temperature stability and flame retardance were improved significantly.⁴⁰ This

process also improved dyeability and imparted hydrophilic surface characteristics to the fibers. Similarly, surface grafting of acrylic polymers onto UHMPE fibers is possible using a low dose rate and low total dose, gamma radiation surface treatment (See Chapter 3).³³ Unlike some of the more prevalent surface modification schemes, the gamma radiation process achieves grafting with complete retention of the excellent UHMPE fiber (Spectra® 1000) mechanical properties. And depending on the glass transition temperature and chemical structure of the polymer graft, fiber/matrix adhesion may be improved by varying degrees relative to the inert PE fiber surface.³³

Kaji *et al.* extended their processing method for ultra-high molar mass, high strength PE fibers using electron-beam (E-beam) irradiation.⁴¹ Grafting of acrylic acid was performed using a pre-irradiation technique in which the fibers are irradiated in a nitrogen atmosphere with an electron beam. After irradiation, the fibers are transferred to a purged acrylic acid aqueous solution containing Mohr's salt as an inhibitor to homopolymerization, and the graft polymerization is subsequently commenced. At doses higher than 1 Mrad, the tensile strength decreases significantly such that at a dose of 20 Mrad the strength drops to less than 65% of the initial value.⁴¹ However, when the fibers are annealed at 70°C after grafting, but prior to exposure to air, the drop in tensile strength is avoided. Likewise, if the fibers are irradiated in the absence of acrylic acid a corresponding decrease in tensile strength is observed.⁴⁰ Again the acrylic acid grafts impart significantly improved dyeability and thermal stability as measured by heat shrinkage measurements and DSC melting point measurements.⁴¹ In particular, the melting point of fibers grafted with 30% acrylic acid that was subsequently converted to

the calcium salt increased from 142°C to 150°C. Yet, heat shrinkage measurements indicated that these fibers exhibited mechanical integrity at temperatures beyond 230°C. Moreover, x-ray evaluations demonstrated that some molecular orientation persisted beyond the melting point.⁴¹ These results are especially attractive in terms of modifying UHMPE fibers for use in high temperature applications as well as high temperature matrices. They also highlight the competition between crosslinking and chain scission mechanisms and the mitigating role that the monomer plays through free radical consumption.

Successful grafting of acrylamide and acrylic acid have also been reported using UV radiation.²⁵ This method is promising for industrial applications since it utilizes a continuous process and because the grafting reaction is most efficient at short irradiation times (10-20 seconds). The acrylic acid-grafted fibers show a three-fold improvement in the IFSS relative to untreated fibers, as determined by the pullout method from an epoxy matrix. The acrylamide-grafted fibers exhibit an IFSS five times greater than the untreated fibers. Both graft materials are expected to chemically react with the epoxy matrix and provide extensive chemical bonding sites along the fiber surface. Neither treatment causes a significant change in the tensile strength, modulus, nor the elongation to failure.²⁵

Fiber surface treatments are an important aspect of polymer-matrix composite performance. Conditions of good adhesion promote stress transfer from the matrix to the fiber and provide a strong interfacial bond. In general, the purpose of surface treatments is to enhance the three essential aspects of adhesion: (i) chemical bonding, (ii) mechanical interlocking and/or (iii) physicochemical bonding. This is accomplished by surface roughening and etching, by increasing the surface free energy of the fiber, by providing

functional groups that are capable of reacting with the matrix and/or by removing a weak boundary layer. With the exception of glass fibers, most of the surface treatments described above are analogous to those commonly employed for carbon, aramid and other high performance fibers.^{30, 44, 45}

Composite Impact Performance

The use of polymer-matrix composites in even more rigorous applications places greater demands on their performance requirements. Not only must these materials provide mechanical support in structural applications, but they must also be able to provide long-term reliability, damage tolerance, and impact resistance. The section above describes the importance of interfacial properties and adhesion between the fiber and matrix for effective and efficient fiber reinforcement.

However, a very strong interfacial bond tends to reduce the toughness of a composite since the chief mechanisms for energy dissipation, e.g., fiber/matrix interfacial failure and fiber pullout, are diminished under these conditions. This phenomenon is well documented for carbon fibers.^{4, 6} Yet, it is also surprisingly true for the inherently tough UHMPE fibers. As described above, weak fiber/matrix adhesion is inherent to untreated UHMPE fibers. This characteristic is vital to anti-ballistic composites, such as Spectra Shield[®], that utilize interfacial debonding as the predominate mechanism of energy dissipation during impact.⁴⁶ Table 2-3 shows the effect of surface treatments that improve adhesion of UHMPE fibers on the impact properties of composites. For example, Ladizesky and Ward showed that an oxygen-gas-plasma treatment improves the ILSS (Table 2-1) of UHMPE fibers by more than 25% but causes greater than a 20% loss in

impact properties.⁴⁷ Similarly, Brown *et al.* showed that ammonia plasma and corona treatments improve the ILSS values of Spectra® 1000 fibers by greater than 100% and 20% (Table 2-1), respectively, but result in a loss in impact performance.¹⁷ Their results also indicate that on a per weight basis, the ballistic properties of UHMPE/epoxy composites are substantially higher than those of aramid composites under the test conditions given.¹⁷ At longer ammonia-plasma treatment times, up to 2 minutes, the fiber/matrix adhesion is further enhanced but a concomitant decrease in the impact strength is realized. And when the ILSS of ammonia-plasma-treated-UHMPE-fiber composites reaches a maximum after 2 minutes of treatment time (Table 2-1), the impact strength continues to decrease up to exposure times of 10 minutes.¹⁷ Long *et al.*⁴⁸ and Tissington *et al.*⁴⁹ also showed that oxygen-gas-plasma treatments enhance the interfacial strength but subsequently limit the damage zone during falling dart impact tests, thus reducing the energy absorbed upon impact. In addition, while the ILSS increases with plasma treatment, the impact energy decreases significantly with increasing fiber/matrix adhesion (Table 2-3). Consequently, the impact properties of fiber-reinforced composites are optimized by different surface modification routes from those used to enhance fiber/matrix adhesion.

The failure of a composite involves the fractures of the load-bearing fibers and the matrix as well as a complex combination of cracks propagated along the fiber/matrix interfaces. Therefore, the toughness of a composite depends on the properties of the constituents as well as the level of adhesion across the interface or interphase. If the basic failure mechanisms and/or the origin of fracture toughness for a given fiber/matrix system

are identified, it is possible to exploit and control these mechanisms. The most ubiquitous failure mechanisms in fiber-reinforced composites that pertain to fiber/matrix interfacial properties include (i) fiber/matrix interface debonding, (ii) post-debonding friction, (iii) fiber fracture and (iv) fiber pullout.⁵⁰ In order to distinguish the individual micromechanisms of toughening it is convenient to consider a model where a crack travelling in the matrix approaches an isolated fiber.

Table 2-3. Effect of Improved Surface Treatment on the Impact Strength of UHMPE-Fiber-Reinforced Composites.

UHMPE Fiber Treatment	ILSS (MPa)		Impact Strength (kJ/m ²)		Ref.
	Untreated	Treated	Untreated	Treated	
plasma (O ₂)	20	25	144 ^{a,c} 61 ^{b,c}	112 ^{a,c} 47 ^{b,c}	47
plasma (NH ₃)	5.7		69 ^{b,c}		17
1 min		11.1		62 ^{b,c}	
2 min		11.8		60 ^{b,c}	
10 min		11.8		54 ^{b,c}	
corona	5.7	7	69 ^{b,c}	63 ^{b,c}	17
plasma (O ₂)	13.2	18	29 (J) ^{b,d}	15 (J) ^{b,d}	48
plasma (O ₂)	9.7	17	38 (J) ^{b,d}	28 (J) ^{b,d}	48
plasma (O ₂)	8.0	14	29.7 (J) ^a	16.0 (J) ^a	49

^aUnidirectional composites.

^bBidirectional (0/90 plain-weave) composites.

^cV₅₀ ballistic impact properties of bidirectional (0/90) composite according to MIL-STD-662 E.

^dFalling dart impact test.

^aModified Charpy impact test (unnotched).

Figure 2-2 shows the stages of crack propagation in a fiber-reinforced composite.⁶ As the crack advances towards the fiber (first stage of Figure 2-2), the lateral stress concentration ahead of the crack tip induces a tensile stress on the fiber/matrix interface

that can lead to fiber/matrix debonding. This is referred to as the Cook-Gordon mechanism.⁵¹ Depending on the interfacial strength, two scenarios are possible. If the interfacial strength is lower than the resultant tensile stress, then interfacial debonding occurs as depicted in the middle image shown in Figure 2-2. If the interfacial strength is high, debonding is prevented and the stress acting on the fiber monotonically increases until the fiber fails in a statistically weak region. This allows the crack to further propagate with minimal energy dissipation, as depicted in the bottom image of Figure 2-2.⁶ Another possible mechanism of debonding occurs when the interfacial strength exceeds the Cook-Gordon tensile stress. In this case, the fiber stress steadily increases until the Poisson's contractions of the fiber invoke stresses that exceed the interfacial shear strength.⁵⁰ Under these conditions debonding aids in the energy dissipation process. Although the Cook-Gordon failure mechanism is regularly observed, longitudinal failure at a weak interface is more commonly caused by the large shear stress component parallel to the fiber developed as a result of the high anisotropy of a high volume fraction composite.⁵² However, the Cook-Gordon mechanism is an important energy dissipation mechanism because of the crack tip blunting which reduces stress concentration ahead of the crack tip as well as its crack arresting feature and a subsequently more tortuous crack path.⁵⁰

After interfacial debonding and/or fiber fracture have taken place, the fiber and matrix move relative to each other as the load is increased and the crack continues to propagate. The post-debonding friction and fiber pullout modes of energy dissipation become operative at this point. And for these modes to contribute significantly to the

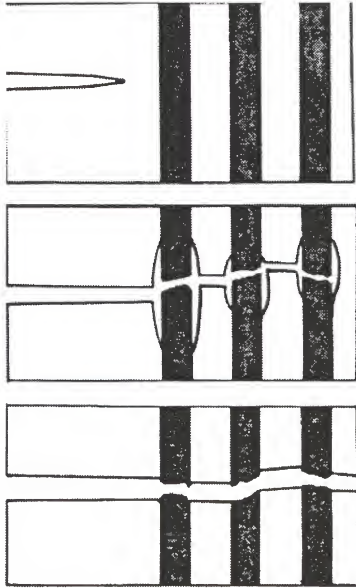


Figure 2-2. Schematic diagram illustrating the approach of the crack (top) and the possible failure mechanisms as the interfacial strength increases. When the interfacial strength is low, debonding occurs by the Cook-Gordon mechanism (middle image), and under conditions of high interfacial shear strength, the crack propagates perpendicular to the fiber axis.^{6, 51}

energy dissipation, weak interfacial properties and correspondingly poor adhesion combined with high frictional bonding are favorable.

Another method of improving the toughness of composites involves the addition of expanding monomers to the matrix to offset polymerization shrinkage. This technique reduces the residual compressive stresses that promote better interfacial bonding and higher frictional forces. The converse of this phenomenon occurs when the fiber coefficient of thermal expansion (CTE) exceeds that of the matrix material. Upon cooling from the curing temperature, a radial tensile stress is produced along the interface. One astounding property of UHMPE fibers is their large positive radial CTE, $13 \times 10^{-5} \text{ mm(mm}^\circ\text{C)}^{-1}$, which is nearly twice that of most epoxy resins. This partly explains the decrease in IFSS values of UHMPE fibers embedded in an epoxy resin with increasing cure temperature shown by Li and Grubb.⁵³ Increasing cure temperature creates a larger residual tensile stress at the interface associated with the large radial CTE of the UHMPE fibers. This characteristic of UHMPE fibers also contributes to their inherently low interlaminar shear strengths and their corresponding effectiveness for toughening composites.

Because of their inherently poor interfacial properties, UHMPE fibers do not typically require surface modification to optimize their impact performance. However, many of the other high performance fibers require special surface treatments in order to improve impact toughness because of their higher interfacial shear strengths. The most common approach towards the optimization of composite toughness involves modification of the interfacial properties using ductile coatings that promote fiber/matrix debonding. This approach was first proposed for fiber-reinforced composites by Broutman and

Agarwal who modeled the influence of a finite interphase layer on the mechanical properties using finite element analysis.⁵⁴ The model showed that the composite modulus increased parabolically with increasing interphase modulus up to a maximum value at which the interphase modulus nearly equals the matrix modulus. As the interphase modulus increases up to the matrix value, the load is transferred from the matrix to the fiber and the composite modulus increases. From the predicted stress distributions, the onset of failure was also predicted, and based on a von Mises failure criterion (i.e., the initiation of composite failure occurs when the distortion energy in any element of the matrix reaches a limiting value), the strength is largely determined by the matrix strength when the interface modulus exceeds 70 MPa.⁵⁴ Thus, at interphase moduli exceeding this value the composite strength is nearly constant. Since the composite modulus changes and the strength is constant over the range of interphase moduli considered, there exists an optimum interface modulus at which the absorbed strain energy is maximized. This value corresponds with an interface modulus of 70 MPa. Hence, the concept of a three-phase, fiber-reinforced composite employing a rubbery interphase originated, although this approach was not novel to particulate reinforced composites.⁵⁵ However, there was an anticipated tradeoff between impact performance and the longitudinal composite modulus and strength as modeled by Broutman and Agarwal.

The role of rubbery interphases on the strength and toughness properties of fiber-reinforced composites has been reviewed by Kim and Mai.⁵⁰ For example, the toughness of Kevlar®-fiber and carbon-fiber-reinforced epoxy composites coated with poly(vinyl alcohol) and silicone rubber, respectively, increased by more than 100%. Similarly, the

toughness of glass-fiber-reinforced epoxy composites realize a significant increase using a low Tg, poly(butyl acrylate) coating.⁵⁰ A surprising result was the negligible effect the low modulus coatings had on the longitudinal tensile strength. In addition to the foregoing surface treatment of fibers, many coating materials have been studied to modify the interfacial properties and eventually to improve the toughness without introducing a large reduction in longitudinal strength and modulus.⁵⁰ The effect of a rubbery coating on the off-axis properties is not mentioned although it is recognized that off-axis properties would suffer because of the low values of interfacial shear strength provided by a weak, rubbery interphase.

Consequently, the intermittent bonding concept was developed. The intermittent bonding concept maintained that if enough of the fiber was left uncoated so as to permit fiber/matrix stress transfer in these regions, the remaining coated segments would provide toughness through the Cook-Gordon mechanism. For example, Atkins achieved a remarkable 400% improvement in the fracture toughness with negligible loss of tensile strength in a unidirectional boron-fiber-reinforced PMC with an 80% coating of polyurethane varnish.⁵⁶ But when the fibers are fully coated the toughness can be further increased to over 500% at the expense of a 25% loss in tensile strength.⁵⁶ Mai and Castino characterized the viscoelastic nature of intermittent, rubbery coatings using a polyurethane coating in Kevlar®-fiber-reinforced epoxy composites.⁵⁷ As expected for a viscoelastic interphase material, the toughness was optimized at low strain rates and high temperatures at which the interphase behaves as a compliant, high friction interlayer. Although chemical bonding is not desirable for maximum toughness, high frictional

bonding contributes to the energy dissipation during fiber pullout.⁵⁸ Likewise, maximum toughening is obtained when the coating is applied over the whole surface area, but at the expense of longitudinal strength and modulus.⁵⁷

Another strategy that was employed to provide an optimal interphase capable of providing both improved interfacial shear strength and impact properties, utilized the electrodeposition of copolymers on the surface of carbon fibers. With this technique, a uniform coating free of pinholes can be achieved since as the polymer layer is formed, the increased electrical resistance of the coating directs further film formation to uncoated areas that are more conducting. Through appropriate polymer coating selection then, it was hypothesized that the interphase would (i) improve shear strength through chemical bonding and (ii) improve toughness by absorbing the energy of impact through deformation.^{6, 59-61} Subramanian and Crasto were the first to try coating carbon fibers using this method.⁵⁹ Although the impact strength was improved with a 50:50 butadiene/maleic anhydride copolymer interphase in a DGEBA-type epoxy matrix, it was altered at the expense of the ILSS. Both SEM and microprobe analysis showed strong evidence of the formation of a thick (ca. 25% of the fiber radius), discrete interphase. However, it was postulated by the authors that the interphase is highly crosslinked and thus, prevents the interpenetration of the matrix and allows debonding at the expense of the ILSS.⁵⁹ Subsequently, a non-crosslinkable interphase was selected using a 40:60 acrylonitrile/methyl acrylate copolymer.⁶⁰ This interphase was compared to an undisclosed commercial oxidative treatment. The impact strength is improved relative to the commercial treatment, however at the expense of the ILSS. It is again postulated that

a weak bonding exists between the interphase and the matrix. Moreover, it is also suggested that the interphase layer is too thick, thus reducing the level of stress transfer between matrix and fiber and causing sticking of the fibers together.⁶⁰ The weight percent of coated polymers ranged from 11%-13%. Assuming an average graft density of 1 g/cm^3 , this would yield a coating thickness of 300-400 nm. In a follow-up study by Crasto *et al.*, an 80:20 ethylene/acrylic acid copolymer was electrocoated with the intention of allowing some matrix penetration and matrix/interphase chemical bonding.⁶¹ The interfacial shear strength was assessed using the single fiber fragmentation test in place of the short beam shear test. This method involves the incorporation of a single fiber in a matrix coupon. Usually a matrix material is chosen such that the strain to failure of the matrix is at least three times higher than that of the fiber.¹⁵ Upon loading the coupon, the stress is transferred to the fiber until the fiber strength is exceeded and fiber failure proceeds. At each point of failure the stress is redistributed between one end of the fiber and the new end created by fracture. Continued application of strain to the coupon results in repetition of this fragmentation process until all the remaining fiber lengths fall short of the critical fiber length, l_c . The critical fiber length represents the length necessary for the shear stress transfer along the fiber to allow build up of fiber tensile stress up to the fiber strength. Thus, an average interfacial shear strength, τ , can be determined from a simple force balance according to

$$\tau = \frac{\sigma_f}{2} \left(\frac{d}{l_c} \right)$$

where d is the fiber diameter and σ_f is the fiber tensile strength. The poly(ethylene-*stat*-acrylic acid) interphase yielded both an increase in the IFSS (63%) and the impact strength (16%), as determined by the notched Izod impact test, compared to untreated fibers.⁶¹ Likewise, a poly(methyl vinyl ether-co-maleic anhydride) interphase provided a synergistic response in terms of the IFSS and the impact strength. However, the discussion was limited to the ethylene/acrylic acid system. The improved adhesion was attributed to the interpenetration of matrix resin and interphase polymer, revealed by electron microprobe analysis of the brominated epoxy resin. The enhanced energy absorption of these interphases was ascribed to their deformable behavior as well as the crack-blunting and crack-deflecting features of the interphase.⁶¹ However, the authors cite the potential to further enhance the interfacial properties by optimizing the coating thickness. It would also be advantageous to clearly elucidate how "deformable" the interphase is by determining to what extent the interphase reacts with the matrix, and/or systematically adjusting the interphase polymer composition so that the importance of the interphase mechanics can be determined as well.

Since the selection of appropriate coating materials for a given composite has traditionally relied on the trial and error method, it is not yet known which coating materials are most suitable for a specific composite system. However, some points of generalization can be drawn with regard to deeming a good coating for improving the toughness of composites: (i) if the coating is fluid or rubbery, a high viscosity coating is preferred because it can increase the frictional shear work during fiber pullout, (ii) if the coating becomes rigid after cure, it should be more ductile and compliant than the matrix and should provide weak bonding at the interface while retaining sufficiently high frictional

bonding, (iii) the thickness of the coating should be kept as small as possible compared to the fiber diameter to eliminate the possibility of reduction in the composite strength and modulus and (iv) partial or complete mixing with the matrix material should be avoided since this would produce composites with scarcely modified interfaces.⁵⁰ Sung *et al.* also suggested that the coating should form and remain in a discrete layer at the interface without reaction with the composite constituents in order to maximize energy absorption.⁶² However, under rigorous processing conditions involving elevated temperatures and high compaction pressures, chemical attachment is more crucial because of the possibility that the coating will be physically removed from the fiber surface. This is an important consideration when designing three-phase composites and it represents one of the main driving forces for the development of chemically grafted interphases. Grafted interphases also represent a method of tailoring the interfacial properties by controlling the graft chemical composition, surface morphology, graft areal attachment density (surface concentration), molar mass and hence, the mechanical and adhesion properties of the interphase.

Tailored Interphases for Optimum Composite Performance

The drawback of the aforementioned grafting methods, i.e., plasma, gamma, E-beam and UV radiation, is that many of these techniques require or employ a high energy source to initiate graft polymerization. This adverse feature manifests itself in the competition between crosslinking and chain scission mechanisms, neither of which are desirable in terms of engineering well-controlled interphases. The high dose rates of E-beam techniques, for example, generally promote chain scission relative to crosslinking

mechanisms.^{63, 64} However, in the presence of acetylene, crosslinking is favored over chain scission for PE fibers.⁶⁴ Likewise, the tensile strength of PE fibers is retained when crosslinking predominates over chain scission, as when the fibers are exposed to E-beam in the presence of monomer.⁶⁵ Process control is also sacrificed because of the complexity of the grafting mechanisms inherent to these methods. During the plasma process a mixture of free radicals as well as ionic species are present and can lead to multiple modes of graft polymerization.³⁸ This lack of control complicates the interpretation of the surface modification results and the elucidation of the role of the interphase in composite performance.

Some insight into the advantage of better defined interphase design was referred to earlier. While Mori *et al.* demonstrated that it is possible to create linear, addition-polymerized interphases by pre-irradiating the fibers followed by exposure to the monomer, Wang *et al.* illustrated the potential advantages of this approach.^{39, 42} They showed that PE-grafted UHMPE fibers provide better reinforcement in terms of modulus and strength than an oxygen-plasma treatment of UHMPE fibers incorporated into a polyethylene matrix. Hence, the advantages of graft/matrix interactions, i.e., entanglements and co-crystallization, provided by PE grafts outweighed the surface modifications associated with plasma, i.e., surface roughening and higher surface free energy. This is analogous to the miscibility improvements that have been achieved using diblock copolymers in polymer blends. In blends, small additions of the diblock copolymer, whose block segments are miscible with one of the individual phases of the blend, stitch the two phases together, significantly reducing interfacial tension and

improving mechanical properties. In fiber-reinforced thermoplastic composites, these additional mechanisms of fiber/matrix adhesion are even more important since the likelihood of covalent bonding is remote. Hence, it is necessary to rely on physicochemical bonding, mechanical interlocking as well as graft/matrix interactions in the form of segmental interactions and entanglements for enhanced adhesion.

Although the majority of the previous examples of grafting involve growth of the grafted chain, a more common approach for carbon and glass-reinforcement fibers involves the attachment of polymer chains. This technique is more plausible using modified glass and carbon fibers because of the high concentrations of reactive species at the surface. End-terminated polymers can subsequently be attached through a chemical reaction between the fiber surface-active species and the graft-polymer termination groups. For instance, DiBenedetto *et al.* attached hydroxy-terminated polycarbonate (PC) and polysulfone (PSf) oligomers to TiCl_4 and SiCl_4 -activated glass fibers.⁶⁶ The interfacial shear strength was subsequently measured using the single fiber fragmentation test. Using this method to assess the effect of graft molar mass, it was shown that the IFSS of SiCl_4 -activated glass fibers grafted with PC oligomer and incorporated in a PC matrix increased with decreasing graft molar mass. The IFSS increased by 0%, 20% and 80% through the graft molar mass range of 25, 4.3 and 1.3 kg/mol, respectively.⁶⁶ Although this might suggest that lower graft molar masses are more effective, in this case, the authors found that the number of grafted PC oligomers decreased with increasing molar mass. Hence, when assessing the efficacy of grafting methods the graft molar mass as well as graft areal density have to be considered. It was also found that the TiCl_4 -activated glass fibers grafted with PSf improved the IFSS, but these systems were severely

damaged upon exposure to boiling water, according to the authors, because of the greater susceptibility of the Ti-O-C bond to hydrolysis.⁶⁶ A final important result showed that the IFSS of the PC-grafted fibers converged to the value of the low molar mass graft after annealing the composites at 230°C for 30 minutes. This phenomenon has been observed by Drzal *et al.* and was attributed to diffusion and adsorption of PC matrix molecules.⁶⁷

A similar result has been determined by Gerard *et al.* using poly (phenylene sulfide) (PPS)-grafted glass fibers embedded in thermoplastic PPS and characterized by the microbond test.⁸ PPS-grafted glass fibers with graft molar masses of 13.6 and 32.4 kg/mol render an IFSS 170% and 210% higher than untreated fibers, respectively. Unlike the result obtained by DiBenedetto *et al.*, the higher molar mass grafts provide more effective stress transfer despite a grafting efficiency over an order of magnitude less than the lower molar mass grafts.⁸

In one of the few studies to consider the exact mechanics of the interphase, Pittman *et al.* studied the effect of polyurethane grafts on the interfacial properties of carbon fibers.⁶⁸ After functionalizing the surface to various degrees with nitric acid, different isocyanate-terminated polyurethane oligomers were grafted to the fiber surface through reactions with surface hydroxyls and carboxyl groups.⁶⁸ The polyurethane oligomers exhibited varying molar masses, 168, 920 and 1444 g/mol, and moduli, 138 MPa, 7.9 MPa and 0.5 MPa, respectively. Likewise, the elongation to failure increases, 29%, 290% and 900%, respectively, with increasing oligomer molar mass. Although the grafting efficiency, G_e , decreases sharply with increasing molar mass (values fit $G_e = KM^a$ where $K = 2750$ and $a = -0.812$) the highest modulus interphase provides a 150%

improvement in impact strength with no loss in the ILSS.⁶⁸ Interestingly, these improvements were cited for interphase thicknesses of only 100 to 150 nm, although the method of determination of this value was not given.⁶⁸ The implication of this result is that the interphase mechanics play an important role in the stress transfer capability of the interphase. Furthermore, the work to failure, i.e. the toughness, of the interphase contributes to the composite toughness and highlights the potential of non-elastomeric interphases that provide other mechanisms of energy dissipation, e.g. through yielding and crazing mechanisms.

The apparent effect of morphology of tethered grafts have raised attention recently to the different modes of conformation related to the variables, graft molar mass and graft areal density. According to theory, tethered grafts attached sparsely to a surface will assume coiled, mushroom-like conformations. As the attachment density (areal density) increases, the tethered grafts will gradually assume a stretched, rather than coiled, conformation and will eventually, as the areal density further increases, extend away from the surface to form a brush-like interphase. The thickness of the grafted layer scales with the molar mass of the tethered polymer, although it scales differently for mushroom-like and brush-like interphases. Consequently, phase diagrams have been constructed that describe binary systems of tethered grafts and matrix chains in terms of the areal attachment density and the relative degrees of polymerization of the tethered polymer.⁶⁹

The effect of areal attachment density and molar mass of grafted chains on glass fibers have been experimentally determined by Lin *et al.*^{70, 71} Polysulfone polymer for tethering purposes was synthesized using bisphenol A and 4,4'-dichlorodiphenyl sulfone

by condensation polymerization. The molar mass was controlled by adjusting the stoichiometry of the reactants. The polysulfone was end-capped by replacing the bisphenol A with an equimolar amount of p-aminophenol. The glass surface was prepared for attachment using 3-glycidoxypolytrimethoxysilane. The areal attachment density was controlled by introducing n-butyltrichlorosilane as a blocking agent prior to the surface attachment of the glycidoxysilane. The chain conformation was predicted using the phase diagram proposed by Aubouy *et al.*⁶⁹ Despite a large amount of scatter, the single fiber pullout test was subsequently used to show that the linear upper bounds of the pullout force-embedded fiber length scatter plots increased with increasing degree of polymerization (N) of the grafted polymer. However, the areal attachment density decreased as the graft molar mass increased. Based on the areal attachment density, it was shown that the low molar mass ($N = 20, 40$) graft/matrix system fell in the region of the phase diagram corresponding with a stretched, unmixed tethered graft. In contrast, the highest molar mass grafts ($N = 60$), exhibiting lower attachment densities, fell in the region corresponding with a stretched and mixed tethered graft.⁷⁰ Thus, the upper bound of the fiber pullout force for these systems was expectedly higher because of the existence of graft/matrix entanglements and higher degrees of interaction. Using the same analysis method, the effect of graft conformation based on varying attachment density was determined by adjusting the level of blocking. In this case, it was shown that the upper bound of the fiber pullout force increased with decreasing areal attachment density.⁷¹ Again, this result was explained in terms of the graft conformation based on the predictions of the phase diagram for the graft/matrix system. The result is not necessarily intuitive since the grafts with the lowest attachment density (0.075 and 0.15 chains/nm²),

i.e., highest degree of fiber surface blocking, yielded the highest pullout force, whereas the grafts with the highest attachment density (0.30 chains/nm^2) and the control (100% blocking) fibers exhibited the lowest pullout forces.⁷¹ Another important result from this study revealed that the polydispersity contributes to adhesion. The polydispersity provides chains with long tails that extend beyond the periphery of the fiber surface. These tails are less densely packed and, therefore, are more accessible to the matrix molecules. Penn *et al.* have demonstrated that fiber pullout force increases with greater graft molar mass polydispersity.⁷² This is an important aspect since very few polymerization mechanisms provide monodisperse molar mass distributions. Moreover, the polymerization mechanism can be selected to optimize the graft polydispersity, e.g., by addition polymerization, and hence begin to design better-controlled interphases and optimize composite properties.

A promising aspect of grafting technology is the possibility of using grafted polymer chains on fibers and fillers to improve the composite toughness as well as adhesion. This concept has been elucidated by comprehensive studies in polymer blends using diblock copolymers.^{13, 73} The driving force for the segregation of the block copolymer to the interface is a reduction in the interfacial tension, and hence, the overall free energy of the system. The mutual solubility between each polymer and its corresponding block of the compatibilizer allows infiltration of the arms of the block copolymer into each phase. Consequently, the sharpness of the interface is reduced and the mechanical properties, i.e., toughness and strength, are significantly improved because of molecular entanglements and other segmental interactions between polymer chains. The molecular processes that a grafted chain can undergo to toughen the interface include chain pullout, scission, and disentanglement. These mechanisms contribute significantly to

the energy dissipation of a propagating crack. In general, when one block of the diblock copolymer is short and the areal attachment density is low, pullout of the short block occurs during interfacial debonding. When both blocks of the diblock copolymer are long and the attachment density is low, chain scission of the diblock copolymer occurs during interfacial debonding. When both blocks are long, crazing, a process that involves chain disentanglement and energy dissipation, occurs during interfacial debonding. For example, Smith *et al.* showed that a block copolymer of polystyrene (PS) and poly(2-vinylpyridine) (PVP) can be used to modify the adhesion properties of a PS/soda-lime glass interface. They demonstrated that the fracture toughness was not enhanced when short PS blocks were used because of failure predominately by chain pullout. However, when both the PS and PVP arms are long ($N > 175$) and the attachment density is large (> 0.10 chains/nm²) the fracture toughness is drastically improved from nearly 0 to 40 J/m².⁷³ This improvement is associated with the effectuation of crazing by the block copolymer. An important aspect to this study is that all of the block copolymers exhibited polydispersities less than 1.1. Thus, it is possible that further enhancements in the toughness are possible utilizing polydisperse grafts as shown by Penn *et al.*⁷²

In a related study, Sha *et al.* evaluated the fracture toughness, G_c , of blends of epoxy and high-impact polystyrene as a function of the attachment density and degree of polymerization of carboxylic acid-terminated polystyrene.¹³ This compatibilizer represents a different approach in which the polymer reacts at one end with one phase of the blend and dissolves in the other to form a graft copolymer at the interface. This scenario is analogous to a polymer chain grafted from the "impenetrable" surface of a reinforcing fiber. Again, no enhancement in toughness was realized compared with a bare

interface when short PS chains ($N = 160$) were used. When the chains are sufficiently long ($N = 410$) to permit entanglements, and the attachment density is high, the interface fails by crazing. As the attachment density increases, the mechanism of interface failure undergoes a transition from scission of the bridging chains to a crazing process followed by craze failure.¹³ However, the maximum grafting density decreases linearly with increasing degree of polymerization. This is analogous to the greater difficulty of attaching grafts with increasing molar mass to fiber surfaces. Most likely this phenomenon is associated with steric hindrance effects. For very long chains ($N = 1860$), even though entanglements exist, the maximum grafting density achievable is very low and such an interface fails by scission so that the toughness is correspondingly low. The optimum interface toughness is achieved with $N \approx 1000$, where both entanglements and a moderate areal density are possible and sufficient to allow failure by crazing.¹³ Once again, the interface polymers are nearly monodisperse with polydispersities always less than 1.2. Based on these results, it is possible to envision a grafting treatment where the properties of the interphase can be tailored to provide both enhanced adhesion and toughening through the intermolecular mechanisms described here.

One of the more promising, less chemically rigorous and hence more commercially viable methods of grafting, involves activation of the surface to yield initiation sites for grafting by addition-polymerization. The advantages of this growth-type grafting process include the control of chemical composition, end-group functionality, molar mass, polydispersity and the inherently higher areal densities compared with the attachment method of grafting for the same graft molar mass.

An effective method of activating olefinic fiber surfaces has been demonstrated by George and Willis, who used a free radical initiator (AIBN) in an oxygen-rich solution of benzene to yield highly hydroperoxidized Spectra® 1000 fabric surfaces.⁷⁴ The hydroperoxide groups were used as bonding sites for the styrene crosslinking reaction in an unsaturated polyester resin. Using chemiluminescence to quantify the thermal decomposition of hydroperoxides, they showed that the concentration increases up to a maximum at a hydroperoxidation time of 60 minutes, decreases up to a time of 90 minutes and increases three-fold relative to the concentration at 60 minutes for a treatment time of 180 minutes.⁷⁴ Fabrics treated for 60 minutes improved the IFSS by a factor of 4 compared with untreated fibers. It is possible to extend this technique by using the hydroperoxidized UHMPE surface as a substrate from which grafting can be effectuated. And depending on the selection of monomers, the use of chain transfer agents, and hydroperoxidation conditions, it is possible to tailor the interphase properties in terms of the modulus, yield strength and shear strength, molar mass and graft density. A similar approach has been studied for glass fibers using copolymers of MPS and butyl acrylate to engineer interphases with varying properties.^{75, 76} However, these copolymers contain pendant silane groups that are used to attach the free-radically polymerized copolymers and form the interphase, and are subsequently crosslinked through hydrolysis reactions with water. Depending on the acidity of the water solution and polymer concentration, the thickness of the interphase may be controlled over the range, 30-150 nm.⁷⁶ Although crosslinking ensures a bound interphase, neither the extent nor the effect of crosslinking on the mechanical properties has been determined. Moreover, the authors postulated that

the poor wetting, as observed by SEM, of the MPS-co-BA interphases by PMMA is related to high interphase crosslink densities that obstruct the inter-diffusion of matrix chains.⁷⁶

A considerable distance has been progressed down the road to designed interphases and yet much is left to be done in terms of fully elucidating the contribution of the interphase to the properties of fiber-reinforced composites. However, the direction initial grafting experiments have taken is encouraging and highlights the exciting potential of fiber-reinforced composites, especially the class of emerging three-phase composites.

CHAPTER 3

SURFACE MODIFICATION OF ULTRA HIGH MODULUS POLYETHYLENE FIBERS BY γ -RADIATION INDUCED GRAFTING

Introduction

Ultra-high modulus polyethylene (UHMPE) fibers exhibit outstanding specific strength and modulus exceeding those of nearly all other fibers available (see Table 1-1).⁵ In addition, their excellent chemical, fatigue, and abrasion resistance make them an attractive candidate for reinforcement of low temperature, high performance composites in marine, biomedical, sporting, and ballistic applications. However, UHMPE fibers are limited by their low working temperature, propensity to creep, and poor adhesion characteristics. The poor adhesion characteristics of UHMPE fibers are attributed to the non-polar nature of the $(-\text{CH}_2-\text{CH}_2-)_n$ backbone and the smooth, low surface energy fiber surface. Without adequate fiber/matrix adhesion, the excellent fiber properties are not fully utilized and optimization of composite mechanical properties is not achieved.

Adhesion is a function of the surface characteristics of the material, i.e., (i) surface topography and roughness, (ii) surface energetics and wettability, and (iii) chemical functionality; and the contribution of each to the level of adhesion is additive.¹¹ Thus, surface treatments that enhance any of these characteristics for UHMPE fibers will improve their reinforcement efficiency in composite systems.

A variety of surface treatments have been devised for UHMPE fibers, utilizing for instance, radio frequency (rf) plasma, chemical, UV-radiation, and electron beam (E-

beam) sources. Surface treatments by plasma exposure in various environments have received considerable attention with mixed results. In particular, Allied Signal uses gas plasma in the commercial production of plasma treated Spectra® fibers. Allied Signal showed that plasma exposure improved flexural properties of epoxy composites, but the fiber tensile strength decreased by approximately 10% with this treatment.¹ Ward *et al.* demonstrated that exposure of UHMPE fibers to oxygen gas plasma increased the surface energy, but caused pitting of the fiber surface.^{2, 11} Additionally, in contrast to the research at Allied, these treated fibers did not improve the tensile properties of unidirectional epoxy composites.

Amination by ammonia and allylamine plasma also leads to similar improvements in the surface characteristics of UHMPE fibers, i.e., an increase in surface energy and wettability, but significantly decreases the mean fiber strength with exposure power.^{5, 34, 35, 38} In a related study, Brown *et al.* showed that ammonia plasma treatment resulted in increases in the interlaminar shear strength (ILSS), fracture energy, as well as flexural properties of Spectra® fabric reinforced epoxy composites.¹⁷ In summary, while the effect of plasma on composite mechanical properties is still being debated, the preponderance of literature indicates that plasma is detrimental to the UHMPE fiber tensile properties.

Several research groups have analyzed the effect of oxidation by wet chemical treatments on the adhesion and wetting characteristics of UHMPE fibers. For instance, Taboudoucht *et al.* reported an increase in the ILSS but cited only minimal improvements in the flexural strength and stiffness of nitric acid treated, UHMPE fiber/epoxy matrix

composites.²¹ Similarly, Ulcay *et al.* showed that chemical treatments with a 50:50 hydrochloric acid/nitric acid solution lowered the strength of UHMPE fibers by approximately 10% and reduced the strength of epoxy matrix composites.²⁴

As has been shown, the existing surface modification techniques involve oxidation, functionalization, polymer deposition, and/or grafting of the fiber surface via high energy exposure and/or aggressive chemical environments. As a result, ultra-high molar mass, highly crystalline polyethylene chains are susceptible to degradation during these treatments. Therefore, the first aim of our work has been to develop a surface modification technique that improves fiber/matrix adhesion but is not deleterious to the mechanical properties of the fiber.

One method of doing this is by radiation induced surface modification using low dose rates and low total dose. Radiation processes such as E-beam, UV, and gamma radiation have been used extensively for surface modification of polymers. Recently, successful grafting of acrylic acid and acrylamide onto UHMPE fibers using E-beam and UV-radiation (320–440 nm) with no loss in fiber tensile properties was reported.^{25, 41} However, the effects of the surface treatment on actual composite properties has not yet been evaluated. E-beam is especially attractive because the extremely high dose rates enable shorter production times for industrial processes. Unfortunately, the high dose rates of E-beam techniques generally promote chain scission relative to crosslinking mechanisms.^{63, 64} Thus, a low dose rate gamma radiation process was selected which has the potential to be extended to the more commercially viable E-Beam grafting process. A gamma radiation process employing low dose rates and low overall doses has been

developed by Goldberg and Kumar for surface grafting of numerous polymers.⁷⁷ The significance of this method is that the surface properties may be modified with no detectable change in the bulk properties of the polymer substrate. For example, gamma radiation induced surface modification has been used on films of low and high density polyethylene, polypropylene, and poly(ethylene terephthalate).⁷⁷⁻⁸⁰ Further, Kaji *et al.* have grafted acrylic acid onto general-use HDPE filaments to impart flame resistance, thermal stability, and hydrophilicity.⁴⁰ However, to our knowledge, there have been no reports concerning surface grafting of UHMPE fibers using gamma radiation. Moreover, numerous surface treatment schemes for UHMPE fibers have been evaluated with regard to fiber/matrix adhesion in thermosets, but few studies have considered this aspect in conventional thermoplastics. Consequently, a method of grafting onto UHMPE fibers using gamma radiation at relatively low dose rates and low total dose has been developed.

UHMPE fibers were grafted with poly(butyl acrylate) and poly(cyclohexyl methacrylate) and incorporated in polystyrene ($T_g = 105^\circ\text{C}$) and a poly(styrene-co-butyl acrylate-co-cyclohexyl methacrylate) statistical terpolymer ($T_g = 44^\circ\text{C}$). In this way, fiber/matrix adhesion was evaluated as a function of the graft mobility at room temperature and matrix ductility, i.e., brittle polystyrene versus a relatively ductile terpolymer matrix. The surface and tensile properties of the UHMPE fibers along with tensile properties and fracture analysis of each composite were characterized using ESCA, FTIR, and mechanical tensile testing.

Experimental

Fibers

Ultra-high molar mass polyethylene fibers, Spectra 1000® and plasma treated Spectra 1000®, were supplied by Allied Signal and Himont Plasma Science, Inc., respectively. Segments of as-received Spectra 1000® (650 denier), 6" in length, were cut and presoaked in test tubes of 33 wt% monomer/chloroform solutions for 84 hours at room temperature to allow diffusion of the monomer into the fiber surface. Prior to use, cyclohexyl methacrylate (CHM) and butyl acrylate (BA) monomers were purified by vacuum distillation. Each filled test tube was purged with argon and subsequently exposed to ⁶⁰Co gamma radiation at a dose rate of 140 rads/min for a total dose of 0.1 Mrad. After radiation grafting, the fibers were immersed in chloroform for 24-48 hours to displace any adsorbed, but not chemically grafted, polymer from the surface. The fibers were then rinsed with methanol and dried at 50°C for 12 hours.

Polymer Matrices

Polystyrene and a poly(styrene-co-butyl acrylate-co-cyclohexyl methacrylate) statistical terpolymer were obtained by bulk polymerization at 60°C for 24 hours using 0.3 wt% azobisisobutyronitrile (AIBN) as initiator. All monomers were purified by vacuum distillation prior to use. The polymers were subsequently dissolved in chloroform, reprecipitated in methanol, filtered and dried at 150°C for 24 hours. The Tg's of polystyrene and the statistical terpolymer were determined by DSC to be 105° and 44°C, respectively.

Composites

Discontinuous fiber reinforced composite laminates were prepared by solution techniques. First, fibers were cut into 10 mm segments and manually dispersed in a 5 wt% polymer/chloroform solution at room temperature. The composite solution was then cast into a glass petri dish, dried under vacuum at 120°C for 12 hours, and compression molded (20-31 MPa) at 120°C into a film approximately 0.35-0.50 mm thick. Finally, the laminate was allowed to slow cool under pressure.

A simple nomenclature for describing the composites according to matrix material, fiber loading, and fiber treatment will be used here. For example, a terpolymer matrix composite, randomly (R) reinforced with 4 wt% poly(butyl acrylate) grafted fibers is designated, TER/R4/BAPE. Table 3-1 lists each composite and the corresponding designation.

Table 3-1. UHMPE Fiber Composite Nomenclature.

Fiber Treatment	Composite Designation	
	Polystyrene Matrix	Statistical Terpolymer Matrix
Untreated	PS/R4/UNPE	TER/R4/UNPE
Poly(butyl acrylate) Grafted	PS/R4/BAPE	TER/R4/BAPE
Poly(cyclohexyl methacrylate) Grafted	PS/R4/CHMPE	TER/R4/CHMPE
Plasma Treated	PS/R4/PTPE	TER/R4/PTPE

Characterization

Surface characteristics of grafted fibers were determined by FTIR/photoacoustic spectroscopy (FTIR/PAS) and electron spectroscopy for chemical analysis (ESCA).

FTIR/PAS analysis was accomplished using a MTEC model 200 photoacoustic detector

(spectral resolution of 8 cm^{-1}) interfaced with a Nicolet 20SX FTIR. Fibers were chopped into approximately 10 mm segments and analyzed in an atmosphere of dry helium gas using 32 sample scans. The FTIR gain and mirror velocity were set at 10 and the photoacoustic gain at 32. ESCA was performed with a Kratos DS800 spectrometer (spectral resolution of 1.1 eV) using $\text{MgK}\alpha$ incident radiation (1.2536 keV). Chopped fibers were washed with ethanol, dried at 50°C , carefully secured to steel mounts using double sided tape, and analyzed.

Each composite was analyzed by DSC prior to mechanical characterization to verify the complete removal of chloroform solvent. Representative samples were taken from the composite films and analyzed from 25 to 150°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen gas flow of 100 ml/min. A decrease in the T_g of the matrix material was indicative of residual solvent because of the plasticizing effect of solvent molecules. In fact, it was found that small concentrations of solvent molecules (1-2 wt% as determined by thermogravimetric/differential thermal analysis) decreased the T_g by nearly 20°C . Composite films containing residual solvent were reheated under vacuum according to the procedure described above. Upon removal of solvent, strips 10 mm wide were cut using a diamond saw under dry conditions. No lubricant was used to prevent modification of the fiber/matrix interface.

Tensile properties were measured using an Instron 1122 equipped with an 890 Newton load cell at ambient conditions. Five samples were tested for each material according to ASTM specifications. UHMPE single filaments were tested according to ASTM D2256 using a gage length of 254 mm and a crosshead rate of 254 mm/min. Terpolymer specimens were characterized according to ASTM D638M (Type M-III die)

because of their high ductility. A crosshead rate of 1.27 mm/min was chosen so that the composite and homopolymer testing rates were comparable. Polystyrene and all composite samples were evaluated using a rectangular geometry (10 X 75 mm) according to ASTM D882. The sample thicknesses were approximately 0.35-0.50 mm as noted above. The initial distance between the grips was 50 mm and the crosshead rate, 5.08 mm/min. The tensile energy to break (TEB) is defined as the area under the stress-strain curve, or

$$\text{TEB} = \int_0^{\epsilon_T} \sigma d\epsilon$$

where σ is the stress at any elongation, ϵ , and ϵ_T is the elongation at failure. The TEB was determined by cutting the stress-elongation curves out of the chart paper, weighing them and computing the energy based on the energy associated with one unit of chart paper.

Fracture surfaces of failed tensile specimens were analyzed by scanning electron microscopy (SEM). A JEOL JSM35CF microscope using secondary electron imaging at an accelerating voltage of 5 kV was employed. The fracture surfaces were coated with Au/Pd for 30 seconds at a coating rate of approximately 5 nm/min prior to analysis.

Results and Discussion

Characterization of Fibers

FTIR

High energy radiation such as ^{60}Co gamma radiation (1.17 -1.33 MeV) may be used to induce surface as well as bulk grafting in UHMPE fibers. If the chemical structure of the graft material is different from that of the substrate, different IR spectra may be

expected due to different bond deformations and corresponding variations in characteristic absorption regions.

The photoacoustic IR spectra of ungrafted and the subtracted result of PBA-grafted fibers minus those of the irradiated-only fibers are illustrated in the top and bottom spectra of Figure 3-1, respectively. Ungrafted, gamma irradiated fibers were used as a reference to account for any oxidation or modification of the polyethylene structure during irradiation. Similarly, the PBA-grafted fibers were analyzed, the irradiated spectrum subtracted and the result compared with PBA homopolymer. Indeed the subtraction spectrum is in good agreement with the IR-spectra for PBA homopolymer. Unlike the gamma irradiated-only fibers (top spectrum), the spectrum of the grafted fibers (spectrum 2) exhibits an additional peak at 1736 cm^{-1} corresponding to C=O bond stretching. The carbonyl peak is attributed to the ester groups in PBA grafts. Similar results were obtained for PCHM grafted UHMPE fibers.

ESCA

ESCA is commonly used to analyze the surface composition of various materials. Depending on the substrate material, the depth analyzed by ESCA may include the first 1-25 nm of surface material, whereas the sampling depth of FTIR is typically 1-10 μm .⁸¹ Hence, ESCA is more representative of the surface composition of the substrate material. This does not suggest that surface grafts are the only material detected by ESCA, nor does it imply that the gamma radiation process only induces surface grafting. Rather, diffusion of monomer into the amorphous portion of fiber during the pre-soak step is critical to successful grafting.⁴¹ In fact, graft material was not detected on fibers that were not pre-soaked.

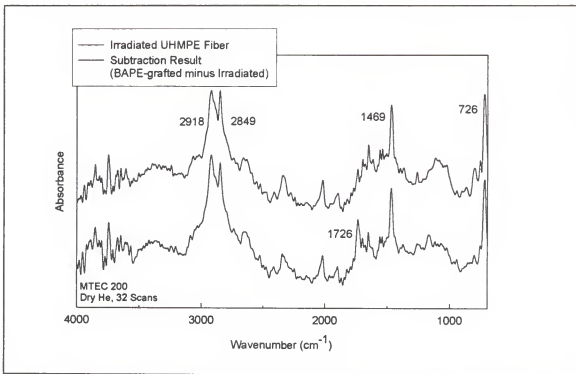


Figure 3-1. FTIR/photoacoustic spectroscopy of UHMPE fibers irradiated in chloroform with no monomer present (top spectra) and the subtraction result of poly(butyl acrylate)-grafted and irradiated UHMPE fibers (bottom spectra).

The high resolution ESCA-C(1s) spectra of the as-received, irradiated (no monomer), and grafted UHMPE fibers are exhibited in Figure 3-2. As was done for FTIR/PAS, the results for fibers irradiated in chloroform with no monomer present were used as a reference to account for any modifications due to irradiation. The main C(1s) peak and a Mg satellite peak are observed at approximately 285 and 277 eV, respectively in all spectra. As is shown, the spectra of the as-received (spectrum 1) and irradiated without monomer (spectrum 2) are essentially the same. This is expected since the fibers and solution were purged to remove oxygen prior to radiation exposure. However, an additional peak is exhibited by the PBA grafted fibers (spectrum 3) with a shift in C(1s) binding energy of approximately 4.5 eV. It has been shown that oxygen induces a C(1s) peak shift to higher binding energies by ca. 1.5 eV per shared electron pair between carbon and oxygen.⁸² Hence, a shift of 4.5 eV is consistent with the presence of ester side groups in poly(butyl acrylate) grafts. Similar results were obtained for PCHM grafted fibers.

ESCA analysis of the plasma treated fibers was also performed but is not included. The oxygen content of plasma treated fibers was comparable to the PBA and PCHM grafted fibers and the nitrogen content was negligible suggesting that an oxygen gas plasma treatment was probably used in their manufacture.

Tensile properties of UHMPE fibers

Radiation grafting involves the hydrogen abstraction and scission of the polyethylene backbone to produce free radicals upon which graft polymerization is initiated.⁶³ However, other competing processes exist. For instance, a radical may recombine, terminate by disproportionation or chain transfer, or attach itself to an adjacent

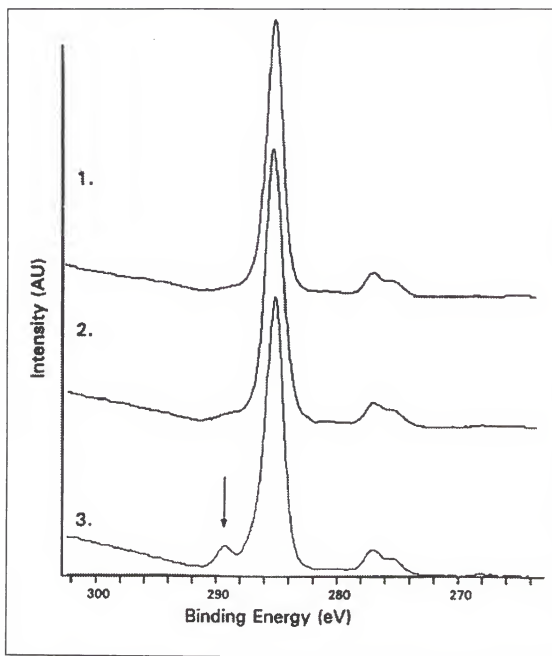


Figure 3-2. High-resolution ESCA C(1s) spectra of (1) as-received, (2) gamma-irradiated in chloroform, and (3) poly(butyl acrylate)-grafted UHMPE fibers. The additional peak in (3) indicates the chemical shift in C(1s) binding energy associated with the ester groups in PBA surface grafts.

chain to form a crosslink junction. Crosslinking is generally viewed favorably since it tends to lead to an increase in mechanical properties. For example, E-beam radiation induced crosslinking enhances the lackluster creep resistance of melt-spun polyethylene fibers.⁶³ Chain scission, on the other hand, may lead to a catastrophic decline in properties, especially for ultra-high molar mass, highly crystalline and oriented polyethylene fibers. Klein *et al.* demonstrated, for instance, that chain scission is more apt to occur at high E-beam radiation doses (9 Mrad) in high molar mass gel spun fibers.⁶³ Similarly, plasma treatment causes a reduction in fiber tensile properties which is generally attributed to a predominance of chain scission.³⁵ Hence, the tensile properties of gamma irradiated UHMPE fibers were measured to monitor this adverse effect.

The tensile properties of plasma treated, gamma irradiated, and grafted UHMPE fibers are illustrated in Figure 3-3. In agreement with previous literature results, plasma treated fibers exhibit a lower strength and modulus than untreated fibers.¹ It is evident that, within error, the high strength and modulus are retained after grafting with PBA and PCHM. Hence, chain scission does not appear to dominate at the relatively low dose rate and low total doses used for our grafting procedure. It is also worth noting that neither an increase in the fiber diameter nor a weight gain was observed following radiation grafting, suggesting that a thin graft layer was formed with no adverse effect on the fiber properties.

Polystyrene Composite Properties

The engineering stress-percent elongation graphs of the polystyrene composites are shown in Figure 3-4. The tensile properties, including the tensile strength, elongation

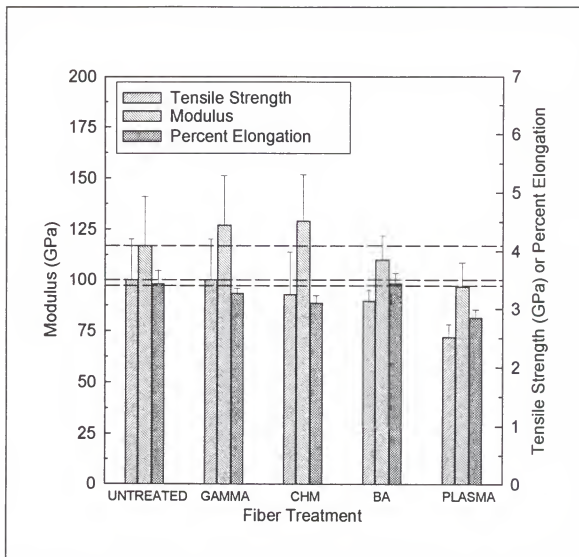


Figure 3-3. Tensile properties of untreated, gamma-irradiated in chloroform only (denoted 'GAMMA'), PCHM-grafted, PBA-grafted and plasma-treated UHMPE (Spectra® 1000) fibers.

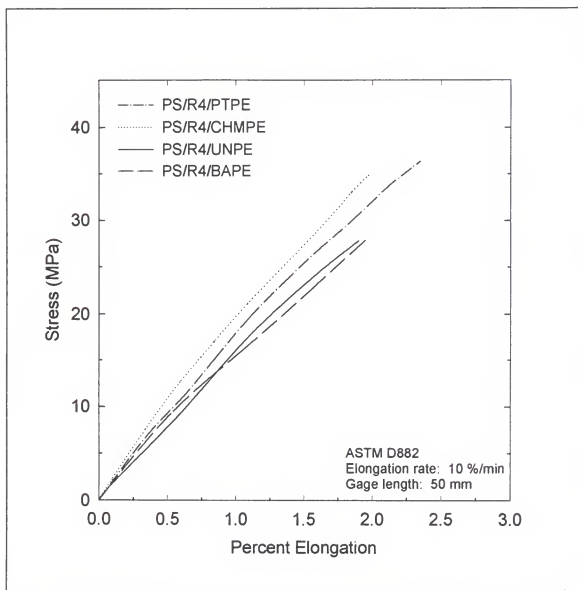


Figure 3-4. The engineering stress-elongation response of polystyrene composites.

to failure, and elastic modulus of polystyrene composites are listed in Table 3-2. In all composites, linear stress-elongation behavior was exhibited up to the point of failure. Failure was followed by fiber pullout, not fiber fracture, suggesting that the fiber length was below the critical fiber length for fiber failure to occur. The critical fiber length is defined as the minimum fiber length required for the fiber stress to be equal to the fiber ultimate strength at the mid-length.³ The addition of as-received and PBA grafted fibers results in a decrease in the stress at break of the composites relative to the polystyrene homopolymer. In contrast, a statistically significant ($\alpha = 0.05$) strengthening effect was observed for PCHM grafted and plasma treated fibers as indicated by a respective 30% and 44% increase in tensile strength. Similarly, PS/R4/BAPE, PS/R4/CHMPE, and PS/R4/PTPE all exhibited nearly a 33% increase in modulus. However, the increase in modulus for PS/R4/BAPE composites was surprising since the rubbery PBA grafts were not expected to enhance reinforcement efficiency.

Table 3-2. Tensile Properties of Polystyrene Composites.

Sample	Tensile Strength (MPa)	Percent Elongation	Elastic Modulus (GPa)
Polystyrene	33.5 ± 1.7	2.2 ± 0.2	1.58 ± 0.10
PS/R4/UNPE	27.7 ± 4.4	2.1 ± 0.4	1.52 ± 0.12
PS/R4/BAPE	29.2 ± 1.9	1.9 ± 0.1	2.11 ± 0.12
PS/R4/CHMPE	36.1 ± 2.0	2.1 ± 0.1	1.99 ± 0.08
PS/R4/PTPE	39.8 ± 3.1	2.5 ± 0.1	1.98 ± 0.12

Results represent the mean and standard deviation for a minimum of five samples.

The SEM micrographs of polystyrene composite fracture surfaces illustrate the relatively poor adhesion in the case of PS/R4/UNPE (Figure 3-5). Improved bonding is

evident in the micrographs for PCHM grafted and plasma treated fibers (Figures 3-6 and 3-7).

The interfacial properties of UHMPE fibers in polystyrene are critical due to the brittle nature of the matrix material. If fiber/matrix adhesion is weak, fibers may act as sites of stress concentration inducing voids at the fiber ends from which crazing of the brittle polymer matrix is initiated.⁸³ Moreover, fibers oriented parallel to the crack plane can act like a rod-shaped microcrack that further accelerates propagation of the crack front.⁸³

In terms of polymer-polymer interactions, molecular mixing is thermodynamically favored when the solubility parameters, δ_1 and δ_2 , of two polymers are similar.⁸⁴ In the absence of hydrogen bonding, immiscibility is likely when $\Delta\delta$ exceeds approximately 0.1.⁸⁵ Typical δ -values for polyethylene and polystyrene are 17.0 and 18.5 MPa^{1/2}, respectively.⁸⁶ Likewise, the accepted δ -value for PBA is 18.5 and a calculated value for PCHM is 18.2 MPa^{1/2}.^{86, 87} Thus, more favorable interactions, i.e., possible graft/matrix molecular entanglement and mixing, between the PBA and PCHM grafted fibers and the polystyrene matrix were anticipated. Figures 3-8 and 3-6 demonstrate that a somewhat tighter interface is achieved for both PS/R4/BAPE and PS/R4/CHMPE. In the case of PS/R4/CHMPE composites, a reinforcing effect was observed as indicated by the increase in strength and modulus. However, a significant reinforcing effect was not expected for the PBA grafted fibers based on the low glass transition temperature of PBA (-45°C). It was hypothesized that the rubbery PBA grafts would not promote stress transfer between the fiber and matrix. As expected, PBA grafted fibers do not reinforce in terms of tensile

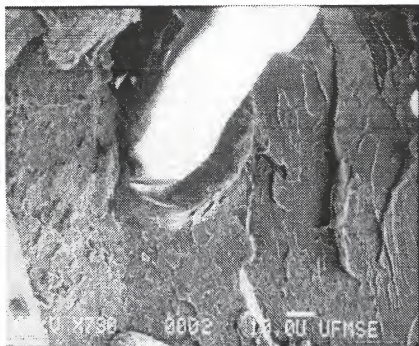


Figure 3-5. SEM micrograph of tensile fracture surface of PS/R4/UNPE composite (magnification x780).

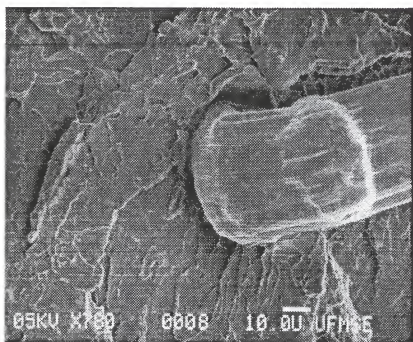


Figure 3-6. SEM micrograph of tensile fracture surface for PS/R4/CHMPE composite (magnification x780).

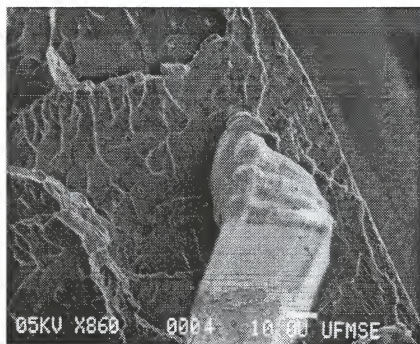


Figure 3-7. SEM micrograph of tensile fracture surface for PS/R4/PTPE composite (magnification x860).

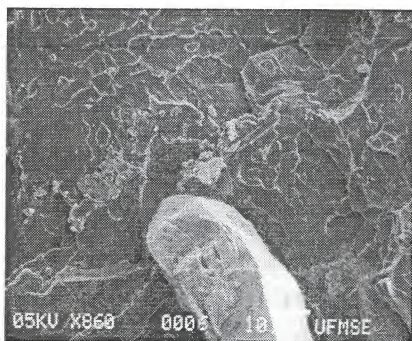


Figure 3-8. SEM micrograph of tensile fracture surface for PS/R4/BAPE composite (magnification x860).

strength. However, PS/R4/BAPE composites display a somewhat surprising increase in stiffness. It was believed that this behavior was related to better wet-out by the PS matrix. However, the dynamic mechanical spectrometry (DMS) response and analysis of these composites corroborates the poor strength-inducing properties of this interphase (see Chapter 4).⁸⁸

The tensile energy to break (TEB) of the polystyrene composites is graphically illustrated in Figure 3-9. The TEB is a measure of toughness since it represents the area under the engineering stress-elongation curve. The PCHM and PT treated fibers demonstrate a toughening effect of 40% and 70%, respectively, compared with the PS/R4/UNPE composite. This result is related to the reinforcing characteristics of these surface treatments. In contrast, the PBA-grafted fibers do not show an increase in the TEB, evidently because the PBA fibers do not provide a reinforcement enhancement. This does not preclude PBA interphases from providing effective impact property improvements, since at the rates of impact testing, the low-T_g interphase can induce energy absorption through yielding and debonding mechanisms (see Chapter 7).

S/BA/CHM Terpolymer Composite Properties

The stress-elongation responses of each of the terpolymer composites are shown in Figure 3-10. Unlike the TER/R4/PTPE and TER/R4/CHMPE composites, the TER/R4/BAPE and UNPE short fiber composites display a greater extent of nonlinear elastic behavior up to failure. In both cases, the deviation from linear behavior occurs near 1.0-1.3 percent elongation. At the point of failure, fiber pullout commences.

The terpolymer composite tensile properties are listed in Table 3-3. All the composites except TER/R4/BAPE displayed linear stress-elongation curves up to failure,

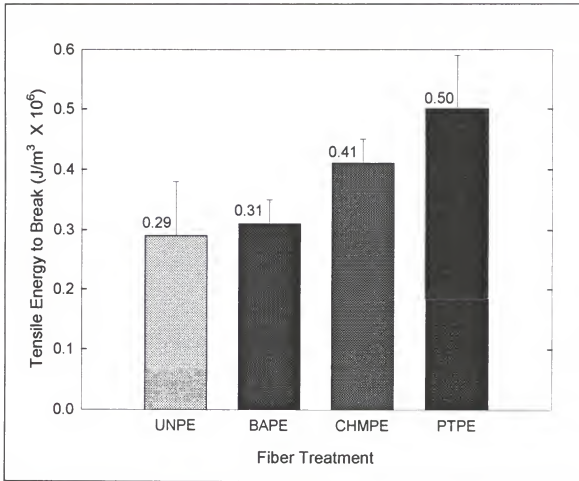


Figure 3-9. Tensile energy to break of PS composites.

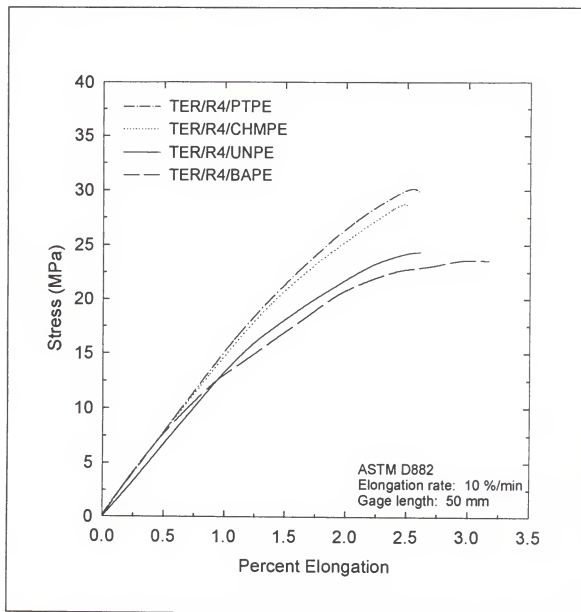


Figure 3-10. The engineering stress-percent elongation response of the S/BA/CHM terpolymer composites.

upon which fiber pullout commenced. In contrast, TER/R4/BAPE composites exhibited a yield point upon which the samples elongated at approximately a constant load until failure. Hence, the tensile strength value reported in Table 3-3 for TER/R4/BAPE represents the yield stress. A reinforcement effect was not observed for the as-received and PBA grafted fibers (TER/R4/UNPE and TER/R4/BAPE, respectively), and in fact a decrease in strength was observed relative to the matrix properties. On the other hand, TER/R4/BAPE composites exhibited a 75% increase in the elongation to failure relative to TER/R4/UNPE composites. A higher level of reinforcement was observed for PCHM grafted and plasma treated fiber composites, TER/R4/CHMPE and TER/R4/PTPE, respectively. In particular, a 26% increase in modulus and 20% increase in tensile strength were observed for TER/R4/CHMPE composites.

Table 3-3. Tensile Properties of S/BA/CHM Terpolymer Composites.

Sample	Tensile Strength (MPa)	Percent Elongation	Elastic Modulus (GPa)
S/BA/CHM Terpolymer	23.6 ± 0.4^a	3.1 ± 0.1^a	1.11 ± 0.35
TER/R4/UNPE	21.5 ± 3.1	2.1 ± 0.5	1.29 ± 0.15
TER/R4/BAPE	21.6 ± 2.4^a	3.5 ± 0.6	1.32 ± 0.08
TER/R4/CHMPE	25.8 ± 2.4	2.2 ± 0.2	1.62 ± 0.14
TER/R4/PTPE	29.7 ± 2.6	2.5 ± 0.2	1.55 ± 0.05

Results represent mean and standard deviation for a minimum of five samples.

^aValues at Yield.

Fracture surfaces of the terpolymer composites are shown in Figures 3-11 through 3-14. Note that TER/R4/UNPE and TER/R4/BAPE (Figure 3-11 and 3-12, respectively) exhibit relatively poor adhesion indicated by the large interfacial gap between the fibers and the matrix. In a ductile matrix such as the terpolymer, fiber reinforcement can be

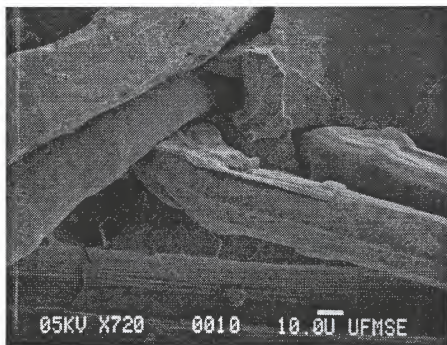


Figure 3-11. SEM micrograph of tensile fracture surface for TER/R4/UNPE composite (magnification x720).



Figure 3-12. SEM micrograph of tensile fracture surface for TER/R4/BAPE composite (magnification x720).

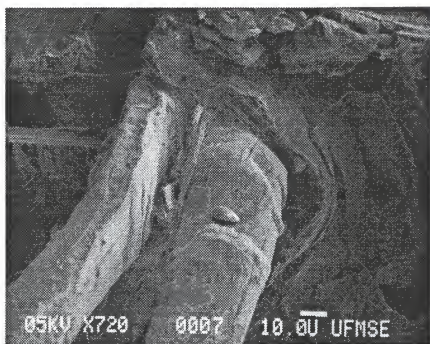


Figure 3-13. SEM micrograph of tensile fracture surface for TER/R4/CHMPE composite (magnification x720)

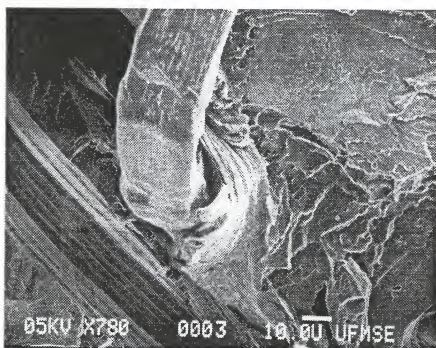


Figure 3-14. SEM micrograph of tensile fracture surface for TER/R4/PTPE composite (magnification x780).

especially ineffective when fiber/matrix debonding is possible due to poor adhesion.⁸³ As a result, fibers may act as sites for stress concentration from which brittle failure is initiated. Figure 3-11 illustrates that brittle failure occurs due to poor bonding in TER/R4/UNPE, in contrast to the plastic deformation of the matrix exhibited by TER/R4/CHMPE and TER/R4/PTPE in Figures 3-13 and 3-14, respectively. The low strength and modulus of TER/R4/UNPE composites are consistent with these observations. Although PBA grafted fibers exhibit poor bonding, they elicit a very different matrix response. Closer examination of Figure 3-12 reveals significant void formation in the interfacial region. It is important to note that this void formation was volumetric, that is, it occurred throughout the composite along the fiber/matrix interface and was observed as a whitening of the fibers during tensile loading. Thus, the large increase in elongation to failure can be attributed to the volume expansion associated with void formation.

The manifestations of such a dramatic increase in the elongation to failure combined with invariable strength and modulus are a significant increase in the tensile energy to break (TEB), i.e., area under the stress-elongation curve, relative to the TER/R4/UNPE composite. Figure 3-15 shows the TEB of the PBA and PCHM-grafted along with plasma-treated UHMPE fiber composites. The TEB is directly related to the fracture energy, G_{Ic} , which may be related to the fracture toughness, K_{Ic} , and modulus, E , by the expression:

$$K_{Ic} = \sqrt{G_{Ic} E}$$

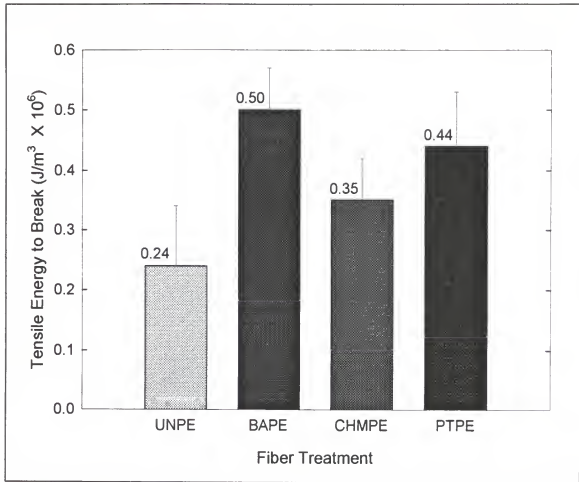


Figure 3-15. Tensile energy to break of terpolymer composites.

A useful assessment of a material's toughness may be obtained with these parameters.⁸³ This demonstrates that the rubbery PBA grafts ($T_g = -45^\circ\text{C}$) are capable of toughening the matrix by inducing an energy dissipative mechanism via void formation in the interfacial region. This same mechanism was observed in PMMA-based, rubber reinforced particulate composites and was associated with improved impact and fracture toughness.⁸⁸ The result is an 100% improvement in the TEB for TER/R4/BAPE composites compared with the TER/R4/UNPE material. The PCHM and PT treated fibers also show a modest increase in TEB, but this is related to the reinforcing effect in terms of the greater modulus and strength.

Enhanced fiber/matrix bonding is observed for TER/R4/CHMPE in Figure 3-13 as indicated by a much tighter interface and plastic deformation of matrix material around the fiber. This is expected since PCHM ($T_g = 84^\circ\text{C}$) is a stiffer polymer with less molecular mobility at room temperature than PBA grafts. Thus, entanglements that form between grafted PCHM chains and matrix molecules are more capable of transferring stress from the matrix to the fiber. The tensile properties of TER/R4/CHMPE composites indicate that more efficient reinforcement is achieved in this system.

Adhesion is a function of the surface topography, chemical functionality, and surface energetics, and each contributes to fiber/matrix bonding.¹¹ The mechanisms which influence adhesion for plasma treated fibers may be completely different from grafted fibers. For example, a decrease in the tensile properties of plasma treated fibers was shown in Figure 3-3. Ward *et al.* have postulated that severe etching causes this decrease in fiber strength due to stress concentration at the pits.^{2, 11} However, etching

may also enhance mechanical bonding. Additionally, ESCA reveals that the oxygen content of plasma treated fibers is comparable to the grafted fibers. Since the atomic oxygen in plasma treated fibers is not contained within polymeric grafts, the functionality of the surface is expected to be vastly different from PBA and PCHM grafted fibers. Considering these differences, the reinforcement efficiency of PCHM grafted fibers is comparable to the plasma treated fibers but PCHM grafts influence fiber/matrix interaction by different mechanisms than plasma treated fibers.

Conclusions

Surface grafting of poly(butyl acrylate) and poly(cyclohexyl methacrylate) onto UHMPE fibers has been achieved by the technique of ^{60}Co gamma irradiation at a relatively low dose rate and low total dose. Unlike some of the more prevalent surface modification schemes, this technique achieves surface grafting with complete retention of the UHMPE fiber mechanical properties.

The effect of the relative molecular mobility of the polymer grafts on the level of fiber/matrix adhesion in thermoplastic matrix composites was evaluated by grafting two materials with very different glass transition temperatures. Poly(cyclohexyl methacrylate) ($T_g = 84^\circ\text{C}$) grafted fibers are an effective reinforcement in the terpolymer and polystyrene matrices. In particular, an approximate 30% increase in strength and modulus were observed. On the other hand, poly(butyl acrylate) ($T_g = -45^\circ\text{C}$) grafts have been shown to induce void formation, i.e., energy dissipation through plastic deformation and volume expansion, at the fiber/matrix interface in terpolymer composites. The latter results in a

75% increase in the elongation to failure and a concomitant 100% improvement in the tensile energy to break.³³

CHAPTER 4

CHARACTERIZATION OF UHMPE FIBER/MATRIX ADHESION BY DYNAMIC MECHANICAL SPECTROMETRY

Introduction

In the previous chapter, it was shown that surface grafting of acrylic polymers onto UHMPE fibers was possible using a low dose rate and low total dose gamma radiation treatment.³³ Unlike some of the more prevalent surface modification schemes, the gamma radiation process achieves surface grafting with complete retention of the UHMPE fiber mechanical properties. Depending on the glass transition temperature and chemical structure of the polymer grafts, fiber/matrix adhesion may be improved by varying degrees relative to the inert polyethylene fiber surface. For instance, UHMPE fibers grafted with poly(cyclohexyl methacrylate) ($T_g = 84^\circ\text{C}$) improved polystyrene composite tensile properties more effectively than lower T_g poly(butyl acrylate) ($T_g = -45^\circ$) grafts. However, the low T_g PBA grafts induced void formation at the fiber/matrix interface of a ductile poly(styrene-co-butyl acrylate-co-cyclohexyl methacrylate) statistical copolymer composite.

Mechanical properties of composites are strongly influenced by the interfacial properties. For example, the fracture toughness of a composite is a function of the matrix failure mechanisms, fiber/matrix interfacial properties, and fiber contributions to energy dissipation, e.g., debonding, fiber fracture, and craze initiation. Friedrich demonstrated that greater fiber/matrix adhesion improves fracture toughness in ductile and brittle

thermoplastic matrix composites.⁸³ Better adhesion enhances the interlaminar fracture toughness, G_{Ic} , and composite strength and stiffness of epoxy matrix composites as well.¹⁷ In contrast, anti-ballistic composites such as Spectra Shield® utilize interfacial delamination as a mechanism of energy dissipation during impact.⁴⁶ Brown *et al.* showed that composite ballistic performance is enhanced by a reduction in interfacial properties, i.e., poor fiber/matrix adhesion.¹⁷ Consequently, a method of achieving a range of interfacial properties is desired. Moreover, the ability to model and subsequently control the interfacial properties according to the desired composite response is very attractive.

Fiber/matrix adhesion is a function of the surface characteristics of the material, i.e., (i) surface topography and roughness, (ii) surface energetics and wettability, and (iii) chemical bonding along the interface; and the contribution of each to the level of adhesion is additive.¹¹ For example, Kodama *et al.* demonstrated that Kevlar® fibers were more effective in a polar matrix, i.e., poly(methyl methacrylate) (PMMA) versus polystyrene, due to a greater degree of polar bonding between the fiber and matrix phases.^{89, 90} Using dynamic mechanical spectrometry (DMS), they showed that the incorporation of fibers lead to a shoulder on the high temperature side of the E'' glass transition peak. The intensity of the shoulder increased with increasing proportion of polar matrix polymer (PMMA) and was attributed to the formation of an interphase due to strong interaction between the Kevlar® fibers and matrix. Ribelles *et al.* also observed additional peaks, peak shifts, and magnitude variations in the $\tan \delta$ response of Kevlar® 49 continuous fiber reinforced poly(ethyl methacrylate) (PEMA) and PMMA.^{91, 92} These effects were attributed to specific interactions between the reinforcing phase and matrix, but not

necessarily to the formation of an interphase. Using a three phase block model, they showed that this behavior could be predicted by including an efficiency factor for the fiber modulus and an additional series term in the rule of mixtures expression.

Several groups have further advanced the idea of an interphase immediately surrounding the reinforcing phase with properties intermediate of the fiber and matrix.⁹³ ⁹⁴ This argument is applied to explain shifts in the T_g of the polymer matrix with the addition of a reinforcing phase. An increase in the T_g is attributed to a lower mobility of the matrix chain segments in the interphase region due to filler/matrix interaction and adhesion. According to this explanation, an increase in the modulus of the interphase juxtaposing the change in T_g is expected. Consequently, researchers have attempted to model the mechanical properties of the composite using a three phase model comprising the filler, interphase, and matrix constituents.

Sideridis modeled the transverse modulus of an E-glass/epoxy composite and compared his results with other theories and experimental values.⁹⁴ The concept of an interphase was incorporated into the transverse modulus using various mathematical functions to describe the transition of the modulus value from that of the fiber to that of the matrix. Although the thickness of the interphase may account for differing degrees of adhesion in this model, the transverse modulus is not sensitive to changes in the mathematical expressions used to describe the interphase modulus.

In contrast, Theocaris *et al.* modeled the longitudinal dynamic modulus of an epoxy matrix with an embedded steel wire, both untreated and oil coated to simulate poor adhesion.⁹³ The interphase modulus, $E_i(r)$, was expressed as an inverse power function in

which the power exponents, n_1 and n_2 , were used to describe the extent of adhesion according to

$$E_i(r) = E_m + E_f \left(\frac{r_f}{r} \right)^{n_1} - E_m \left(\frac{r_f}{r} \right)^{n_2}$$

where the subscripts f and m refer to fiber and matrix properties, respectively, and r represents the radial distance from the center of the fiber. The ratio n_2/n_1 is a measure of the quality of adhesion. Under conditions of perfect adhesion in which $n_2/n_1=1$, the interphase modulus decreases continuously from the value of E_f and asymptotically approaches E_m with values always greater than the value of E_m . When $n_2/n_1 < 1$, the interphase modulus decreases more rapidly from the value of E_f and at $r=r_o$ reaches a minimum value, $E_{i,min}$, which is less than the value of E_m . Subsequent work by Theocaris and Ponirides utilizing related expressions were used to evaluate E-glass fiber reinforced thermoplastics such as polyethylene, polystyrene, and PMMA.⁹⁵ However, surface modification of the glass fibers was not attempted and the differences in the adhesion coefficient, n , between composites were relatively insignificant. Moreover, no significant changes in the dynamic mechanical response of the composites was observed. Therefore, the most promising model for evaluating the extent of fiber/matrix adhesion based on dynamic mechanical spectrometry is the three phase block model as described by Ribelles *et al.* 91, 92

The purpose of this portion of the work was to evaluate the validity of the three phase block model for a series of grafted UHMPE short fiber reinforced composites. UHMPE fibers were grafted with poly(cyclohexyl methacrylate) and poly(butyl acrylate)

using gamma radiation and incorporated as short fibers (10 mm) in polystyrene and a poly(styrene-co-butyl acrylate-co-cyclohexyl methacrylate) statistical terpolymer as described previously (12). The reinforcement efficiency of UHMPE fibers was characterized by tensile tests and DMS. The $\tan \delta$ response was simulated according to the three phase model and the level of fiber/matrix adhesion quantified as a function of surface treatment. In addition, high density polyethylene films were treated according to the same procedure and characterized by contact angle measurements.

Experimental

Materials

Ultra-high molar mass polyethylene fibers, Spectra 1000® and plasma treated Spectra 1000®, were generously supplied by Allied Signal and Himont Plasma Science, Inc., respectively. As described previously, grafting was accomplished by pre-soaking Spectra 1000® (650 Denier) fiber segments in monomer/chloroform solutions and subsequently exposing the fibers while in solution to ^{60}Co radiation at a dose rate of 140 rads/min for a total dose of 0.1 Mrad.³³ Consequently, PCHM and PBA grafted Spectra® fibers, plasma treated, and untreated fibers were evaluated as reinforcement fibers. Polystyrene and the poly(styrene-co-butyl acrylate-co-cyclohexyl methacrylate) (1:1:1) statistical terpolymer were bulk polymerized from purified monomers.

Discontinuous fiber reinforced composite laminates were processed by solution techniques. First, fibers were cut into 10 mm segments and manually dispersed in a 5 wt% polymer/chloroform solution at room temperature. The composite solution was then cast into a glass petri dish, dried under vacuum at 120°C for 12 hours, and upon removal of all

solvent, was compression molded (10,000-15,000 pounds) at 120°C into a film approximately 0.35-0.50 mm thick. The laminate was allowed to slow cool under pressure. Finally, strips 10 mm wide were cut using a diamond saw under dry conditions. The use of lubricant was avoided to prevent modification of the fiber/matrix interface.

A simple nomenclature for describing the composites according to matrix material, fiber loading, and fiber treatment will be referred to herein. For example, a terpolymer matrix composite, randomly (R) reinforced with 4 wt% poly(butyl acrylate) grafted fibers is designated, TER/R4/BAPE. Table 4-1 lists each composite and the corresponding designation.

Table 4-1. Randomly Oriented, UHMPE Fiber-Reinforced Composite Nomenclature.

Fiber Treatment	Composite Designation	
	Polystyrene Matrix	Statistical Terpolymer Matrix
Untreated	PS/R4/UNPE	TER/R4/UNPE
Poly(butyl acrylate) Grafted	PS/R4/BAPE	TER/R4/BAPE
Poly(cyclohexyl methacrylate) Grafted	PS/R4/CHMPE	TER/R4/CHMPE
Plasma Treated	PS/R4/PTPE	TER/R4/PTPE

Characterization

Each composite was analyzed by DSC prior to mechanical characterization. Representative samples were tested from 25 to 150°C at a heating rate of 10°C/min under a nitrogen gas flow of approximately 100 ml/min. A decrease in the T_g of the matrix material indicated residual solvent due to the plasticizing effect of solvent molecules. It was found that small concentrations of solvent (1-2 wt% as determined by TG/DTA)

decreased the T_g by nearly 20°C. Composite samples containing residual solvent were redried prior to testing.

Tensile properties were measured at ambient conditions using an Instron 1122 equipped with a 200 pound load cell. Five samples were tested for each material according to ASTM specifications. The terpolymer was characterized according to ASTM D638M-84 (Type M-III die) due to its high ductility. A crosshead rate of 1.27 mm/min was chosen to maintain comparable testing rates for the composite and homopolymer samples. Polystyrene and all composite samples were evaluated using a rectangular geometry (10 X 75 mm) according to ASTM D882-83. The sample thicknesses were approximately 0.35-0.50 mm as noted above. The initial distance between the grips was 50 mm and the crosshead rate, 5.08 mm/min.

Dynamic mechanical spectrometry was performed using a Seiko DMS200(FT) tension module interfaced with a Seiko SDM5600H Rheostation. Rectangular sample dimensions as described for the tensile specimens were used. Samples were tested from 150 to 170°C at a heating rate of 0.75°C/min under a dry nitrogen gas flow of approximately 200 ml/min. The samples were analyzed at frequencies of 0.1, 1, and 10 Hz, of which, the spectra at 1 Hz are presented.

Contact angle measurements of high density polyethylene films were taken using a Rome-Hart goniometer. HDPE films were used since surface characterization could be easily performed and relative differences in the surface properties of untreated and treated films could be obtained. The films were prepared by compression molding HDPE pellets (Dow Chemical) at 150°C between Kapton® sheets under a load of 10,000-15,000 pounds. The films were surface treated according to the grafting procedure described for

the fibers. An additional film was treated without monomer to evaluate the effect of gamma radiation on the surface properties of polyethylene. Prior to analysis, the films were cleaned by submerging each in methanol for approximately 1 minute and air drying. Each film was subsequently secured to the top of an open plastic dish filled with distilled water so that the bottom side of the film was completely immersed. An air bubble was then carefully introduced to the immersed side of the film using a syringe. Five contact angle measurements were taken for each film and the average and standard deviation reported.

Results and Discussion

Tensile Properties of Polystyrene Composites

The tensile properties of the polystyrene composites are listed in Table 4-2. The stress at break of PS/R4/BAPE composites is significantly ($\alpha=0.05$) lower than the polystyrene homopolymer. In contrast, a statistically significant strengthening effect was observed for PS/R4/CHMPE and PS/R4/PTPE composites as indicated by a 30% and 44% increase in tensile strength, respectively. Similarly, both the PS/R4/CHMPE and PS/R4/PTPE composites exhibited nearly a 33% increase in modulus. However, the increase in modulus for PS/R4/BAPE composites was not anticipated based on the low T_g of PBA (-45°C). Also listed in Table 4-2 is the tensile energy to break (TEB). The TEB is defined by the area under the stress-elongation curve and is a useful assessment of a material's toughness (13). The TEB of PS/R4/PTPE composites is significantly higher than PS/R4/UNPE and unreinforced polystyrene. However, PS/R4/CHMPE composites do not yield a significant increase in the TEB.

Table 4-2. Tensile Properties of Polystyrene Composites.

Material	Tensile Strength (MPa)	Percent Elongation	Elastic Modulus (GPa)	Tensile Energy to Break (MJ/m ³)
Polystyrene	33.5 ± 1.7	2.2 ± 0.2	1.58 ± 0.10	0.39 ± 0.05
PS/R4/UNPE	27.7 ± 4.4	2.1 ± 0.4	1.52 ± 0.12	0.29 ± 0.09
PS/R4/BAPE	29.2 ± 1.9	1.9 ± 0.1	2.11 ± 0.12	0.31 ± 0.04
PS/R4/CHMPE	36.1 ± 2.0	2.1 ± 0.1	1.99 ± 0.08	0.41 ± 0.04
PS/R4/PTPE	39.8 ± 3.1	2.5 ± 0.1	1.98 ± 0.12	0.50 ± 0.09

Tensile Properties of Terpolymer Composites

The mechanical properties of the terpolymer composites are listed in Table 4-3. Although the average strength of both the TER/R4/UNPE and TER/R4/BAPE composites are lower than the yield strength of the matrix, the decrease is not significant ($\alpha=0.05$). On the other hand, a significant increase in modulus and stress at break was observed for TER/R4/CHMPE and TER/R4/PTPE composites. In particular, a 26% increase in modulus and 20% increase in strength was observed for TER/R4/CHMPE relative to TER/R4/UNPE composites. Scanning electron microscopy (SEM) of these materials showed improved fiber/matrix adhesion and plastic deformation of the matrix extending from the interface into the bulk of the matrix.³³ Conversely, the TER/R4/BAPE composites did not show better fiber/matrix adhesion, but extensive void formation around the fiber/matrix interface was evident. While testing this material a whitening around the fibers could be seen due to void formation. Consequently, TER/R4/BAPE composites exhibited a 75% increase in the elongation to failure and a 100% increase in TEB relative to TER/R4/UNPE composites. The implications of this toughening effect as well as a more thorough explanation of the SEM micrographs were described in Chapter 3.³³

Table 4-3. Tensile Properties of S/BA/CHM Terpolymer Composites.

Material	Tensile Strength (MPa)	Percent Elongation	Elastic Modulus (GPa)	Tensile Energy to Break (MJ/m ³)
S/BA/CHM Terpolymer	23.6 ± 0.4	3.1 ± 0.1	1.11 ± 0.35	—
TER/R4/UNPE	21.5 ± 3.1	2.1 ± 0.5	1.29 ± 0.15	0.24 ± 0.10
TER/R4/BAPE	21.6 ± 2.4	3.5 ± 0.6	1.32 ± 0.08	0.50 ± 0.07
TER/R4/CHMPE	25.8 ± 2.4	2.2 ± 0.2	1.62 ± 0.14	0.35 ± 0.07
TER/R4/PTPE	29.7 ± 2.6	2.5 ± 0.2	1.55 ± 0.05	0.44 ± 0.09

Contact Angle Measurements of HDPE Films

Adhesion is a function of surface topography, chemical functionality and surface energetics. The latter is generally associated with the propensity of the matrix to wet the fibers. A high energy surface will generally provide better wet-out than a lower energy surface. Based on the surface properties reported for polyethylene, poly(butyl acrylate) and poly(cyclohexyl methacrylate), it was hypothesized that the wetting characteristics of treated and untreated fibers would not vary significantly. For example, Wu reported a surface tension of 35.7 mJ/m² for linear polyethylene ($M_w = 67,000$ g/mol) and a value of 33.7 mJ/m² for poly(butyl acrylate) ($M = 32,000$ g/mol).⁹⁶ In addition, Rapoza and Horbett measured very similar captive bubble contact angles for polyethylene and poly(cyclohexyl methacrylate), 77.0° and 81.0°, respectively.⁹⁷

In order to assess the differences in wettability of the various fibers following radiation-induced grafting, the contact angle, θ , of HDPE films was measured using the captive bubble technique (Figure 4-1). Although surface tension is a function of polymer molar mass, for our purposes this effect is negligible. For example, Wu measured a

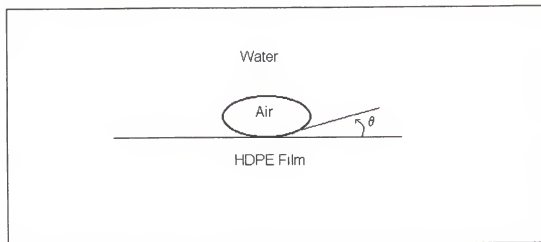


Figure 4-1. Schematic of the contact angle, θ , measured by the captive bubble technique (Note that the image is inverted).

surface tension of 35.7 mJ/m^2 for linear polyethylene ($M_w=67,000 \text{ g/mol}$), and reported a value of 36.8 mJ/m^2 for polyethylene with molar mass extrapolated to infinity.⁹⁸

Likewise, Chaoting *et al.* reported a surface tension of 34 mJ/m^2 for ultra-high molar mass fibers ($M_w=3,500,000 \text{ g/mol}$) with a draw ratio comparable to the Spectra® fibers.⁹⁹

Thus, it is possible to evaluate the wetting characteristics of UHMPE fibers using HDPE films. The contact angles of untreated, gamma irradiated, and PBA and PCHM-grafted HDPE films are listed in Table 4-4. The contact angle of PBA and PCHM-grafted films are significantly ($\alpha=0.05$) lower than the untreated and irradiated film (with no graft). However, radiation exposure does not cause a significant reduction of the contact angle.

Chaoting *et al.* also showed that oxygen gas plasma treatment of UHMPE fibers increased the surface tension to a value of 60 mJ/m^2 corresponding with a contact angle for water equal to 37° .⁹⁹ This value is listed in Table 4-4 for comparison purposes.

Therefore, improved wetting may be expected for the PBA and PCHM-grafted fibers but

not to the same extent as the plasma treated material. This supports the conclusion that the improvements in the mechanical properties of grafted fiber-reinforced composites is related to the interaction of polymer grafts with matrix molecules, not simply improved wetting characteristics.

Table 4-4. Contact Angle of HDPE Films Measured by the Captive Bubble Technique.

HDPE Films	Average Contact Angle, θ
HDPE	56 ± 4
HDPE gamma irradiated	53 ± 5
HDPE-g-PBA	48 ± 2
HDPE-g-PCHM	48 ± 4
Plasma treated UHMPE fiber ¹	37

DMS and Three Phase Modeling of Composites

As described above, Kodama and Karino observed a second loss modulus (E'') peak in the DMS of Kevlar® reinforced blends.⁹⁰ The additional E'' peak was attributed to fiber/matrix interactions based on a rise in its magnitude as the polarity of the matrix was increased. Ribelles *et al.* observed similar features in Kevlar® reinforced PEMA and PMMA and modeled this behavior using a three phase model.⁹¹ This model was employed here to further elucidate the effect of gamma radiation induced surface grafts on UHMPE fiber adhesion.

The dynamic mechanical spectra of TER/R4/CHMPE and the terpolymer are shown in Figure 4-2. The storage modulus, E' , of the matrix at 25°C is 2 GPa, which is characteristic of a glassy polymer. E' decays approximately 3 orders of magnitude over the temperature range of 27°C to 77°C corresponding to a T_g of 44°C for the terpolymer.

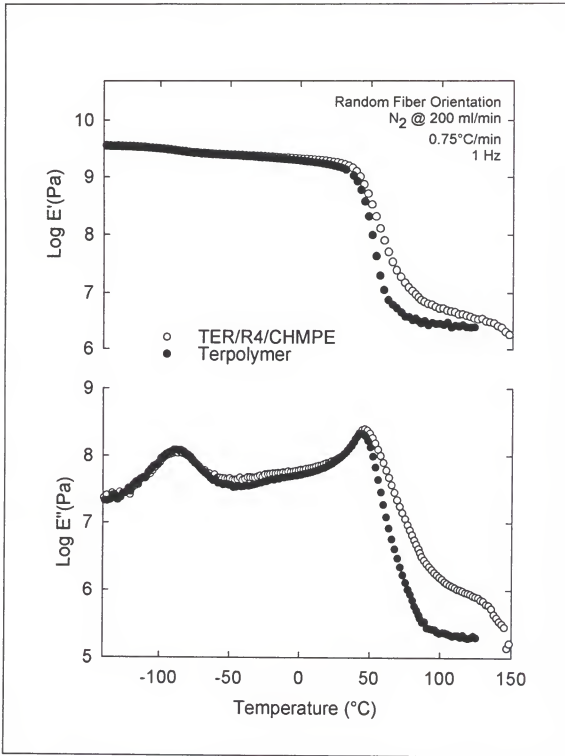


Figure 4-2. The storage modulus (E') and tan delta temperature profiles of the terpolymer and the TER/R4/CHMPE composite ($v_f = 0.04$, $l_f = 10$ mm).

The storage modulus of TER/R4/CHMPE follows a similar trend except that the onset of decay of the storage modulus is shifted to a slightly higher temperature and the modulus in the rubbery plateau is increased. A further decay in the storage modulus of TER/R4/CHMPE occurs at approximately 137°C corresponding to the melting of UHMPE fibers. The storage modulus of both materials below 27°C increases with decreasing temperature. The same general trends are observed for the other terpolymer composites, the polystyrene sample, and the polystyrene composites except that the glass transition region for polystyrene composites is superimposed with the onset of melting of the polyethylene crystals.

The tan delta spectra in the lower portion of Figure 4-2 show a peak near -80°C. This corresponds with the axial and equatorial chair-chair conformational mechanism of cyclohexyl methacrylate present in the terpolymer matrix.¹⁰⁰ The high temperature tan delta peak near 37°C is associated with the glass transition of the matrix. The loss dispersion associated with the cyclohexyl ring is independent of fiber reinforcement whereas the loss associated with the T_g is dependent on fiber reinforcement. Similar trends were observed for the other terpolymer composites as well as the polystyrene and the polystyrene composites. However, the low temperature tan δ peak is not present for the polystyrene materials. Although the dynamic mechanical properties have only been discussed for a frequency of 1 Hz, each of the transitions discussed above has been characterized for a series of frequencies (0.1, 1, and 10 Hz) and, as expected, each exhibits frequency dependence.

The tan δ spectra of the terpolymer matrix composites are plotted as a function of temperature in Figure 4-3. The phase angle, δ , which is a measure of the lag between the

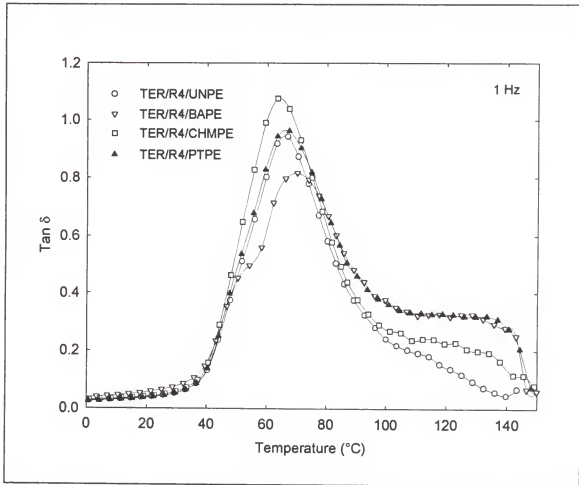


Figure 4-3. The measured $\tan \delta$ spectra of the terpolymer composites for the various fiber surface treatments ($v_f = 0.04$, $l_f = 10$ mm).

stress of the sample and the applied cyclical strain is a measure of the viscoelastic properties of the material. The $\tan \delta$ may be expressed as a function of the loss and storage moduli according to

$$\tan \delta = \frac{E''}{E'}$$

Figure 4-3 illustrates the dependence of the $\tan \delta$ response on the fiber surface condition. For instance, the TER/R4/BAPE spectrum is characterized by the formation of a shoulder on the low temperature side of the main peak and a shift in the peak temperature to a higher value. The response of each material at temperatures greater than the main peak temperature, i.e., $>90^{\circ}\text{C}$, is also strongly influenced by the surface condition of the UHMPE fibers. It is evident that the magnitude of $\tan \delta$ in this region increases with surface treatment relative to the untreated fibers.

Major differences are observed in the $\tan \delta$ response of the polystyrene composites (Figure 4-4). The spectra of PS/R4/CHMPE shows a more Gaussian-like $\tan \delta$ response with a large peak magnitude whereas the other composites exhibit shoulders and much smaller peak magnitudes. PS/R4/BAPE and PS/R4/PTPE composites, in particular, display prominent shoulders along the low temperature side of the main peak. The response at temperatures greater than the main peak temperature do not differ significantly. This was expected since the T_g of polystyrene superimposes the melting temperature of polyethylene crystals.

As discussed above, Ribelles *et al.* observed similar behavior for Kevlar® reinforced PEMA and PMMA.^{91, 92} Using a three phase model originally developed by

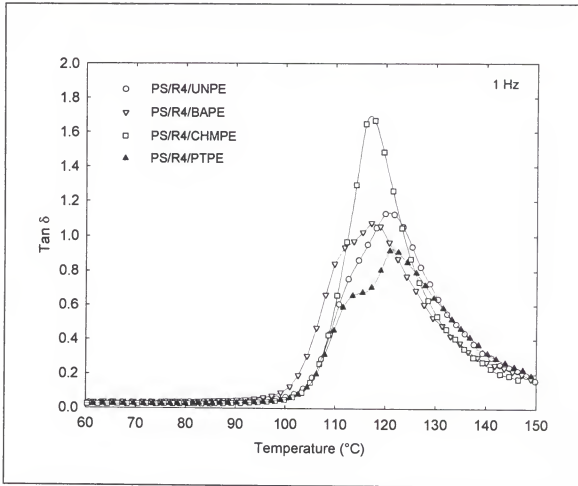


Figure 4-4. The measured $\tan \delta$ spectra of the polystyrene composites for various fiber surface treatments ($v_f = 0.04$, $l_f = 10$ mm).

Takayanagi, they successfully modeled the observed $\tan \delta$ response.¹⁰¹ Similarly, the differences in the $\tan \delta$ response of the polystyrene and terpolymer composites is explained using a thermomechanical block model. The block, as depicted in Figure 4-5, is composed of three regions, two of which are in parallel (the fiber and matrix) and an additional block that is in series. The volume fraction of each phase is written in terms of the volume fraction of fibers in the composite, Φ_f . The "skin effect", fiber misorientation, and other factors which permit additional strain are accounted for by the series term, λ . The skin effect is attributed to the non-uniform strain at the surface relative to the bulk as a result of clamping the sample at the surface. The term K accounts for imperfect fiber/matrix adhesion, discontinuous fiber reinforcement, and other causes of diminished reinforcement efficiency.

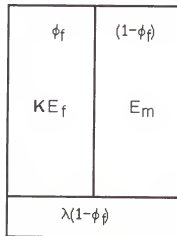


Figure 4-5. The three-phase block model, where the f and m subscripts refer to fiber and matrix attributes, respectively. Volume fraction is denoted by ϕ and the terms K and λ are used to describe the reinforcement efficiency and the amount of matrix material in series, respectively.

Thus, the complex composite modulus can be described by a combination of the parallel and series rule of mixtures expressions according to

$$\frac{1}{E_c^*} = \frac{1-\xi}{K \Psi E_f^* + (1-\Psi) E_m^*} + \frac{\xi}{E_m^*}$$

from which

$$\tan \delta_c = \frac{(M'' E_m' + M' E_m'')(\xi M' + (1-\xi) E_m') - (M' E_m' - M'' E_m'')(\xi M'' + (1-\xi) E_m'')}{(M' E_m' - M'' E_m'')(\xi M' + (1-\xi) E_m') + (M'' E_m' + M' E_m'')(\xi M'' + (1-\xi) E_m'')}$$

where

$$M' = K \Psi E_f' + (1-\Psi) E_m'$$

$$M'' = K \Psi E_f'' + (1-\Psi) E_m''$$

and

$$\Psi = \frac{\Phi_f}{1-\xi}$$

$$\xi = \lambda(1-\Phi_f)$$

The subscripts c, f, and m refer to composite, fiber, and matrix properties, respectively. The E^* denotes the complex modulus while E' and E'' refer to the storage and loss modulus components, respectively. The volume fraction of the matrix and fiber

phases are represented by Φ . Consequently, ξ equals the volume fraction of "skin" which is the fraction of matrix phase in series. The volume fraction of fibers in parallel excluding the skin material is represented by Ψ . The quantity $(1-\Psi)$ then represents the amount of matrix material in parallel. Thus, when λ is zero, the volume fraction of skin (ξ) is zero, and Ψ is equal to Φ_f .

Prior to simulating the dynamic mechanical response of the composite, the thermomechanical profile of both the fiber and matrix were determined. A $\tan \delta$ value of 0.05 was measured for the 650 Denier bundle of UHMPE fibers (Spectra® 1000). The loss modulus of the composite was subsequently calculated by substituting the measured modulus of UHMPE fibers (approximately 120 GPa) into the equation for $\tan \delta_c$. DMS was also performed on both polystyrene and the terpolymer. The corresponding E' and E'' temperature profiles were used to simulate the $\tan \delta$ response. Finally, K and λ values were chosen to provide the best fit between the simulated and actual $\tan \delta$ responses.

Intuitively, λ should be equal for all the composites since each contains an equal fraction of randomly oriented short fibers. However, the solutions to the model were obtained by finding the best fit between the simulated and actual $\tan \delta$ response curves. Consequently, λ varies slightly for this set of samples. The small variations indicate small differences in fiber dispersion between samples. If the $\tan \delta$ response is solved keeping λ constant, there is poor agreement between the simulated and actual spectra. Figures 4-6 and 4-7 are included to illustrate this point. Figure 4-6 shows the simulated $\tan \delta$ response for the terpolymer composites ($\lambda = 0.08$). Although the spectra match the actual response shown in Figure 4-3 relatively closely, the (K, λ) solutions do not provide the

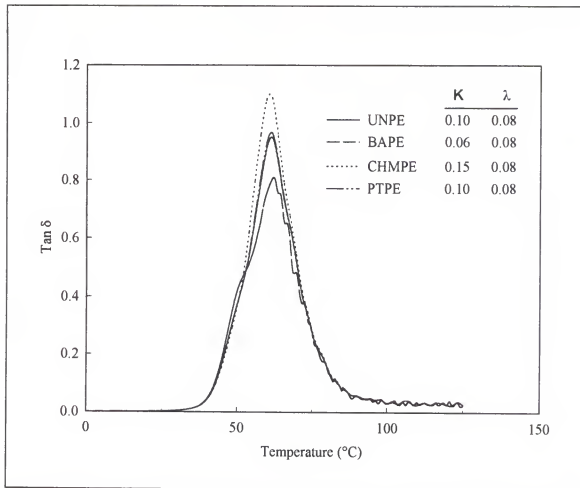


Figure 4-6. The simulated $\tan \delta$ response of the terpolymer composites when λ is fixed ($\lambda = 0.08$).

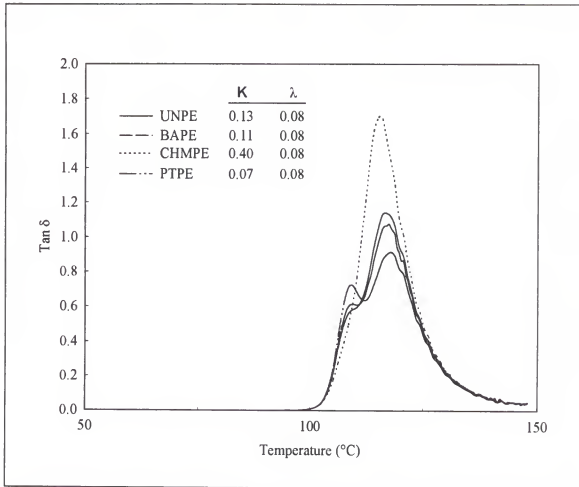


Figure 4-7. The simulated $\tan \delta$ spectra of the polystyrene composites when λ is fixed ($\lambda = 0.08$).

best fit. The simulated $\tan \delta$ response for the polystyrene composites are shown in Figure 4-7 ($\lambda = 0.08$). These spectra illustrate more clearly the importance of solving for both K and λ . For instance, there is very poor agreement between the PS/R4/PTPE simulated spectrum and the actual response (Figure 4-4). Hence, individual (K , λ) solutions were determined for each composite.

The effect of discontinuous fibers on fiber reinforcement efficiency is well documented in terms of the critical length.^{3, 102, 103} The critical length is the fiber length at which stress transfer is sufficient to cause fiber failure and is inversely proportional to the fiber/matrix interfacial strength, i.e., the level of adhesion. As discussed above, tensile specimens show fiber pullout during tensile failure rather than fiber fracture. Below the critical length, inefficient stress transfer prevents utilization of the excellent UHMPE fiber properties. This effect and others responsible for inefficient reinforcement are compensated for by the term K . K -values ranging from 0 to 1 were computed where $K = 1$ indicates perfect adhesion and $K = 0$, poor fiber/matrix adhesion. The simulated $\tan \delta$ spectra and the corresponding (K , λ) values for the terpolymer composite materials are shown in Figure 4-8. Comparison of these spectra with Figure 4-3 shows that close agreement between the experimental data and the model are achieved. For example, the shoulder in the TER/R4/BAPE spectra is accurately replicated and the breadth and magnitude of each of the peaks is successfully modeled. However, the high temperature response of the terpolymer composites is not adequately modeled exposing a shortcoming of the three phase model. A more applicable model for temperatures

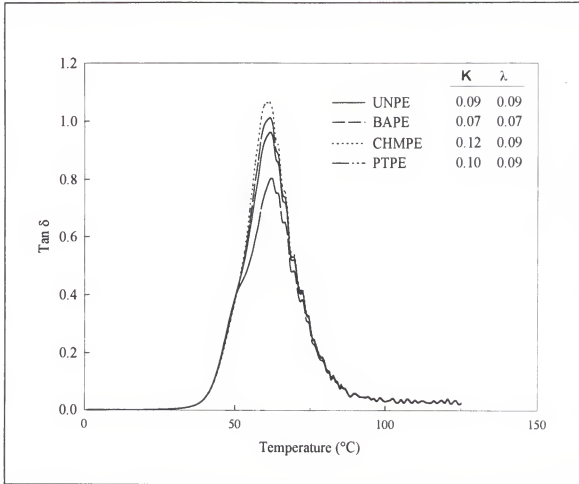


Figure 4-8. The simulated $\tan \delta$ spectra of the S/BA/CHM terpolymer composites. (K , λ) solutions that yield the best fit with the measured response are tabulated for each fiber surface treatment.

exceeding the T_g of these polymers is a modified Kerner equation, which is used to describe the modulus of elastomers filled with a rigid reinforcing phase.¹⁰⁴

The simulated spectra of the polystyrene composites (Figure 4-9) successfully replicate the dramatic variations in the actual $\tan \delta$ response (Figure 4-4). These features include the prominent shoulders formed on the low temperature side of the glass transition peak of PS/R4/BAPE and PS/R4/PTPE composites as well as the weak shoulder of PS/R4/UNPE. The Gaussian-like response of PS/R4/CHMPE is also easily accounted for by the model using appropriate (K , λ) values. Although values of λ in the range 0.03-0.13 have been chosen, lower λ -values have been used for continuous fiber reinforced composites.⁹¹ However, higher values would be expected for a discontinuous, randomly oriented fiber composite since the volume fraction of reinforcement is dramatically lower and additional strain in series would be expected to occur throughout the specimen. The higher K -values, i.e., improved adhesion, computed for PS/R4/CHMPE and PS/R4/PTPE are in agreement with the tensile properties listed above and the fracture behavior reported in chapter 3.³³ For example, the K -values for PS/R4/CHMPE and PS/R4/UNPE are 0.30 and 0.13, respectively. Moreover, the level of reinforcement for PCHM grafted and plasma treated fibers is comparable. The same general trend is displayed by the terpolymer composites.

Conclusions

Surface grafting of poly(butyl acrylate) and poly(cyclohexyl methacrylate) onto UHMPE fibers has been achieved by the technique of ^{60}Co irradiation at a relatively low dose rate and total dose. The PCHM ($T_g = 84^\circ\text{C}$) grafted fibers are an effective

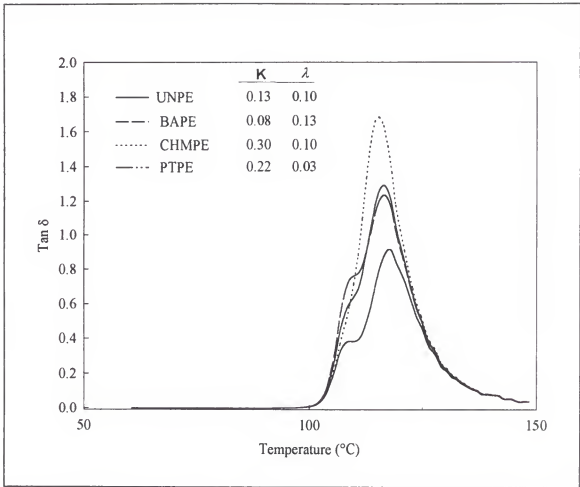


Figure 4-9. The simulated $\tan \delta$ spectra of polystyrene composites. (K, λ) solutions are tabulated for each fiber surface treatment.

reinforcement in the terpolymer and polystyrene matrices. In particular, an approximate 30% increase in strength and modulus was observed. On the other hand, PBA ($T_g = -45^\circ\text{C}$) grafts induce void formation and energy dissipation through plastic deformation and volume expansion at the fiber/matrix interface in terpolymer composites. The latter results in a 100% increase in the tensile energy to break.

A thermomechanical block model encompassing a fiber reinforcement efficiency parameter, K , and a series term, λ , was utilized to simulate the $\tan \delta$ response. Consequently, the DMS response of each composite was successfully modeled by selecting suitable K and λ values. The resulting fiber reinforcement efficiency values were consistent with the tensile properties and fracture surface features. ¹⁰⁵

CHAPTER 5

ANNEALING OF ULTRA-HIGH MODULUS POLYETHYLENE FIBERS: TENSILE PROPERTIES AND IMPLICATIONS OF FIBER MORPHOLOGY

Introduction

Ultra-high modulus polyethylene (UHMPE) fibers are produced commercially by gel-spinning a 6% solution of ultra high molar mass ($>10^6$ g/mol) polyethylene. The ensuing drawing process orients the chains in an extended chain conformation and yields a highly crystalline polymeric fiber (84-93%) with excellent mechanical properties. The specific strength, for instance, of Spectra® (Allied Signal) UHMPE fibers surpasses that of most other commercial fibers (Table 1-1). Some other outstanding features of UHMPE fibers are their low moisture absorption, abrasion resistance and comparatively high elongations to failure. The latter property is useful for providing high impact resistance for composite laminates, including use in conjunction with stiffer carbon fibers to produce hybrid laminates with improved impact resistance. As a result, UHMPE fibers are finding increasing application in marine and ballistic composites. However, their use in high performance structural and load-bearing composites is curbed because of their inherently poor creep resistance, poor adhesion, and low service temperature. Consequently, polyethylene has endured exhaustive studies in the areas of creep and adhesion.

On the other hand, the thermal stability of UHMPE fibers is often overlooked except to say that the melting point is rather low. According to Mallick, the safe manufacturing temperature for composites containing UHMPE fibers is below 125°C

since the fibers exhibit a rapid reduction in strength near the melting point.³ However, the manufacturer of Spectra® fibers (Allied Signal) recommends a processing temperature below 93°-104°C, although many researchers use the melting temperature (147°C) as the benchmark below which PE fibers are processible.⁴⁶ This lack of consensus over the optimum processing temperature is demonstrated using the DSC thermal response curve of UHMPE fibers plotted in Figure 5-1. Overlaying the DSC curve is the frequency of maximum processing temperatures cited in each of the adhesion studies performed on UHMPE fibers. The figure shows that nearly half (16 of 37) of the citations involve processing temperatures exceeding both the manufacturers recommendation and the initial melting (90°C) of polyethylene crystallites in UHMPE fibers. Thus, the first objective of this paper is to expose the far reaching implications of this kind of oversight, especially in terms of our understanding of the reinforcement and adhesion properties of UHMPE fibers.

A significant portion of the research done on UHMPE fibers is related to improving adhesion. The most ubiquitous methods of quantifying adhesion involve pullout or microbond tests. These methods evaluate the adhesion of a single filament to the matrix, usually a heat-cured thermoset material, by gripping both the fiber and matrix and measuring the load required to initiate debonding. The interfacial shear strength (IFSS) is represented as the force divided by the area of fiber/matrix contact. Unfortunately, the UHMPE fibers are characterized by rather low shear strengths themselves because of the extended chain conformation. The 100-fold difference between the shear and tensile

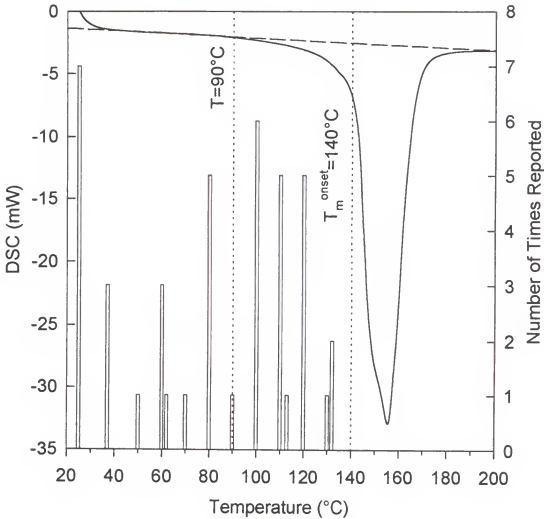


Figure 5-1. The DSC thermal response of UHMPE fibers is shown in the top portion of the figure. Indications of polyethylene chain reorganization are observed beginning at 90°C. The onset temperature of melting is equal to 140°C. The bars represent the number of times UHMPE fibers were processed at a particular temperature. Nearly half of the studies, to date, involve processing temperatures above the recommended value of 90°C.

moduli is believed to induce fiber rupture by shear failures and corresponding fibrillation in UHMPE fibers.⁹⁹ Consequently, it is necessary to develop some means of characterizing the type of debonding, whether interfacial or cohesive fiber failure. For all practical intents and purposes, a cohesive UHMPE fiber failure represents the maximum attainable improvement in fiber/matrix adhesion. But if this criteria is sensitive to the processing temperature, it becomes a moving target and makes any interpretation of adhesion tests qualitative at best.

The numerous articles on gas plasma treatment demonstrate the sensitivity of pullout type tests to the fiber mechanical properties. For example, Chaoting *et al.* showed that despite the fact that over 87% of the adhesion is related to chemical and mechanical bonding, extended plasma treatments that enhanced these two mechanisms of bonding also cause severe structural damage to the fiber surface.⁹⁹ Consequently, the tensile strength decreases. Although the highly oxidized and pitted fiber surface provides ample opportunity for chemical bonding and mechanical interlocking, there is a reduction in the interfacial shear strength (IFSS).¹⁰⁶ This is attributed to a decrease in the UHMPE fiber mechanical properties upon extended plasma treatment, which leads to cohesive fiber failure during the pullout test. The same result is expected if the mechanical properties change as a result of processing at too high a temperature.

A common approach taken to analyze the IFSS is to plot the pullout force versus the fiber/matrix contact area. A linear regression of the resulting data points tracks through the origin and yields the IFSS value via the slope of the line. In most cases, the data does not track through the origin. This is attributed to fiber end effects, lateral

pressure of the gripping device and cohesive failure of the fiber.^{26, 107} Thus, our understanding of adhesion is strongly affected by the interpretation and validity of these types of tests along with our recognition that morphological changes may occur during the processing stage. Our objective in this study is to report the thermal stability of UHMPE fibers after annealing at various temperatures.

This paper will chronicle a series of annealing experiments done on UHMPE fibers. The thermal stability of the fibers is evaluated using tensile tests and differential scanning calorimetry (DSC). Optical microscopy is used to monitor changes in the fiber diameter caused by shrinkage. In addition, wide angle x-ray diffraction (WAXD) results are reported and scanning electron microscopy (SEM) is used to image the fiber fracture surface. The effect of annealing on the fiber mechanical properties is discussed in terms of the morphology of polyethylene, reorganization of PE molecules, taut-tie molecule concentration (TTM) and structure-property relationships of polymeric materials.

Experimental

Fibers

UHMPE, Spectra® 900, fibers were generously supplied by Allied Signal, Inc. (Richmond, Va.). Per their suggestion, the UHMPE fibers were washed in methanol for two hours prior to use. The reported tensile strength, modulus and elongation to failure are 2.7 GPa, 120 GPa and 3.5%, respectively. The density of UHMPE fibers is 0.97 g/cm³ and the reported diameter of the fibers is 38 μ m.

Annealing Treatments

Single filaments and bundles of the UHMPE fibers were loosely secured and annealed for two hours in a VWR convection oven. The oven was calibrated prior to use. Following the annealing treatment, the fibers were allowed to air quench. The annealing temperatures include 80°C, 100°C, 120°C, 130°C, 137°C and 140°C. An annealing time of 2 hours was selected since it represents an average processing time for both thermoset cure and short fiber mixing and extrusion profiles.

The diameter of the fibers was measured after annealing to calculate shrinkage. Measurements were made using a Bausch & Lomb optical microscope.

Differential Scanning Calorimetry

The thermal response curves of the UHMPE fibers were obtained using a Seiko model DSC 220C (heat-flux type). The DSC was interfaced with a Seiko 5600H Rheostation that was used to collect and assimilate the data. The sample-side thermocouple and DSC signal were calibrated using indium, tin, and bismuth standards. A heating rate of 10°C/min was utilized, and a dry nitrogen atmosphere was maintained at a flow rate of approximately 100 ml/min. Each sample was prepared by measuring approximately 10 mg of fiber, and subsequently run in crimped aluminum pans. The enthalpy of melting and peak and onset melting temperatures were quantified using the thermal analysis software.

Tensile Tests

Fiber tensile properties were measured using an Instron 1122 mechanical tester with an 890 Newton load cell. Single UHMPE filaments were tested according to ASTM

D2256 at a rate of 100%/min and a gage length of 254 mm. Approximately 10 fibers per treatment were tested in order to ascertain any statistical significance. An average fiber diameter of 38 μm was calculated based on the fiber denier of 650 and 60 filaments per bundle.

X-Ray Diffraction

Wide angle x-ray diffraction (WAXD) patterns of the UHMPE fibers were collected using a Phillips APD 3720 wide-angle x-ray diffractometer with $\text{Cu-K}\alpha$ radiation. The fiber bundles were wrapped around glass slides and positioned so that the fiber c-axis aligns along the ϕ -axis of the diffractometer. All data was collected at room temperature over the 2θ range of 20° to 60° at a scan rate of $2^\circ/\text{min}$.

SEM of the Fiber Tensile Fracture Surfaces

SEM images of the tensile fracture surfaces were obtained using a JEOL JRL-6400 scanning electron microscope. The samples were prepared by carefully attaching the fracture specimens to a sample holder using double-sided tape. Subsequently, the samples were carbon coated for approximately 30 seconds and imaged.

Results and Discussion

Characterization of Annealed UHMPE Fibers

The tensile properties of UHMPE fibers annealed at various temperatures below the melting point are shown in Table 5-1. The effect of annealing on the tensile strength, modulus and elongation to failure are also presented graphically in Figures 5-2, 5-3 and 5-4, respectively. The mechanical properties are strongly influenced by the annealing treatments. In particular, the tensile strength decreases dramatically when treated above

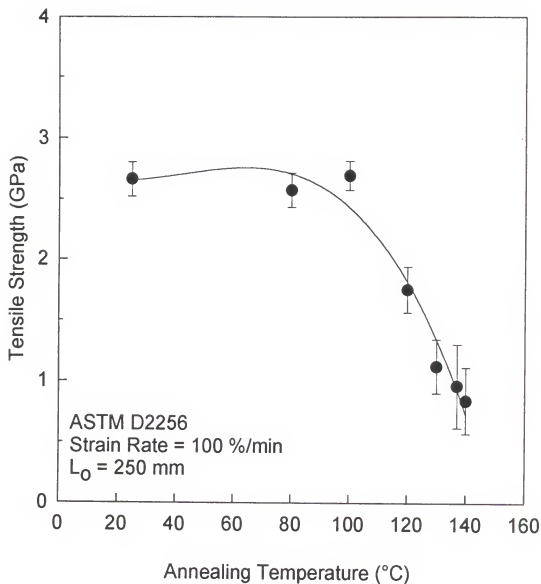


Figure 5-2. The tensile strength of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation (n=10).

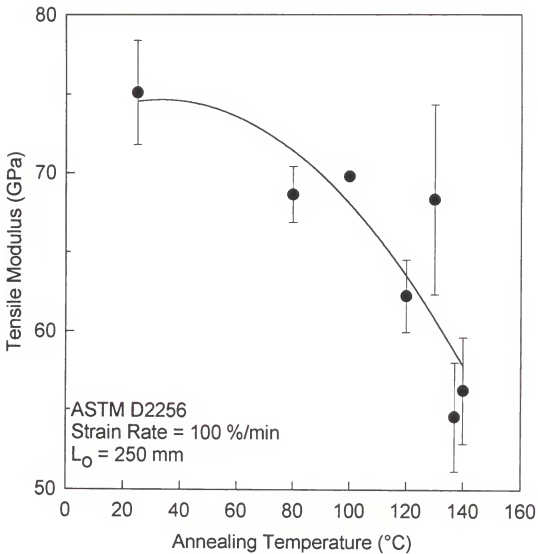


Figure 5-3. The tensile modulus of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation ($n=10$).

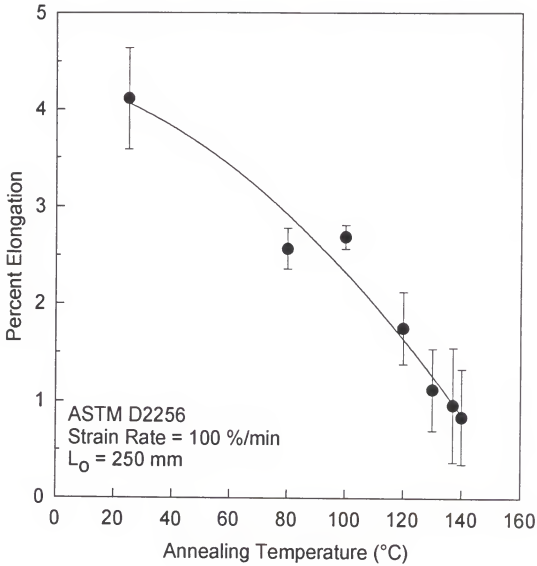


Figure 5-4. The percent elongation to failure of UHMPE fibers versus annealing temperature (annealing time=2 hrs). The error bars represent one standard deviation ($n=10$).

100°C. Below 100°C, the variations in strength are not statistically significant ($\alpha=0.05$) relative to the 25°C sample (Note that the 25°C sample represents the as-received fiber). When the fibers are annealed at 140°C, the measured onset of melting temperature (this temperature will henceforth be referred to as T_m), a decrease in strength of 68% is observed. The modulus-temperature relationship exhibits a similar trend to the strength behavior. The modulus shows a statistically significant decrease when annealed at 120°C followed by a marked decrease in the elastic modulus above an annealing temperature of 130°C. Fibers annealed near T_m show a decrease in elastic modulus of only 25%. In contrast to the modulus and strength, the elongation to failure decreases monotonically with temperature. After annealing at the T_m , an overall 80% reduction in the elongation is observed.

Table 5-1. Tensile Properties of Annealed UHMPE Fibers.

Annealing Temperature	Tensile Strength (GPa)	Elongation (%)	Elastic Modulus (GPa)
25°C	2.66 ± 0.14	4.1 ± 0.5	75.1 ± 3.3
80°C	2.57 ± 0.14	2.6 ± 0.2	68.7 ± 1.8
100°C	2.69 ± 0.12	2.7 ± 0.1	69.8 ± 0.1
120°C	1.75 ± 0.19	1.8 ± 0.4	62.2 ± 2.3
130°C	1.12 ± 0.22	1.1 ± 0.4	68.3 ± 6.0
137°C	0.96 ± 0.34	0.96 ± 0.6	54.6 ± 3.4
140°C	0.84 ± 0.27	0.84 ± 0.5	56.2 ± 3.4

The fact that the strength and elongation to break, properties both very flaw sensitive, are much more affected by annealing led us to explore the notion that the annealing treatment may induce flaw sites through changes in surface morphology. However, Tapping Mode™ atomic force microscopy of the fiber surfaces revealed negligible changes in the surface morphology. Fiber shrinkage was also suspected,

however, optical microscopy showed that the diameter remained constant across the annealing temperature range.

DSC was used to characterize the effect of annealing on the thermal properties of UHMPE fibers. It was thought that annealing might cause the T_m to drop and/or decrease the bulk crystallinity. The enthalpy of melting (ΔH_m) values are reported in Table 5-2 for the as-received, methanol washed, and annealed fibers at 137°C and 140°C. Three samples each of the as-received and MeOH washed fibers were tested to obtain a standard deviation of the enthalpy measurement. The change in ΔH_m is not statistically significant ($\alpha=0.05$) between the as-received and MeOH washed fibers. Moreover, the increasing trend in ΔH_m for the annealed fibers is not anticipated nor does it reflect a decrease in the percent crystallinity ($\Delta H^{100\%}=292.9 \text{ J/g}$ at 141°C). DSC analysis also shows that the T_m does not decrease with annealing. Hence, the drastic reduction of the mechanical properties of UHMPE fibers after annealing is not explained by changes in the bulk crystallinity or the overall thermal response as measured by DSC.

Table 5-2. Enthalpy of Melting (J/g), ΔH_m , of UHMPE Fibers after Annealing at 137°C and 140°C.

As-Received	MeOH Washed	137°C	140°C
245.4 ± 12.6	258.2 ± 5.2	261.5	271.5

WAXD of UHMPE fibers shows several distinctly identified peaks across the 2θ range of 10° - 60° . The peak locations, corresponding d-spacings and the intensity ratio, $I/I_{\max}$, for as-received and fibers annealed at 100°C and 137°C are listed in Table 5-3. It is evident that the fibers consist of a mostly orthorhombic structure with the exception of a

Table 5-3. WAXD Results for the Annealing of UHMPE Fibers.

As-Received			100°C Annealing Treatment			137°C Annealing Treatment		
2-Theta (°)	d-spacing (nm)	I/I _{max}	2-Theta (°)	d-spacing (nm)	I/I _{max}	2-Theta (°)	d-spacing (nm)	I/I _{max}
19.4 (M010) ^a	0.456	2.0	—	—	—	—	—	—
21.5 (110)	0.412	100	21.8	0.407	100	21.8	0.406	100
24.0 (200)	0.371	25	24.3	0.367	27	24.3	0.366	28
30.1	0.296	1.3	30.3	0.294	1.5	30.6	0.292	1.3
36.4 (020)	0.247	3.0	36.6	0.246	3.2	36.5	0.246	3.4
38.3 (120)	0.235	0.21	38.6	0.233	0.34	38.6	0.233	0.41
40.7 (310)	0.221	2.0	41.1	0.220	2.2	41.1	0.220	2.4
44.0 (220)	0.206	1.0	44.2	0.205	1.2	44.3	0.204	1.2
49.2 (400)	0.185	0.31	49.4	0.184	0.43	49.5	0.184	0.54
52.2	0.175	0.49	52.7	0.174	0.51	52.7	0.174	0.62
57.1	0.161	0.34	57.6	0.160	0.33	57.4	0.160	0.38

^a Numbers in parentheses denote the (hkl) plane indices corresponding with the orthorhombic crystal structure of polyethylene. "M" denotes the monoclinic crystalline phase.

single, low intensity peak associated with the monoclinic crystalline phase and a few low intensity reflections of the triclinic phase.^{108, 109} The monoclinic phase forms under transverse compressive stresses and melts at approximately 100°C, which explains the disappearance of this phase upon annealing.¹¹⁰ With the exception of this observation, it is apparent that the annealing treatments induce only negligible changes in the diffraction pattern of these fibers. Likewise, the amorphous halo that ranges from 15° to 25° is negligible in all three of the fibers analyzed. The surprising fact that no bulk morphological changes are observed over the time frame of the annealing experiments led us to formulate a distinct hypothesis based on the unique morphology of gel-spun UHMPE fibers.

Implications of the Morphology of UHMPE Fibers

The extent of orientation produced by the gel-spinning and drawing of UHMPE yields a fiber comprised almost entirely of chain extended molecules.¹¹¹ There is general agreement that the hierarchical structure of UHMPE fibers comprises macrofibers that are in turn composed of microfibrils (~2-15 nm in diameter) oriented along the fiber longitudinal axis.^{112, 113} A general schematic of the arrangement of microfibrils is given in Figure 5-5. The figure is analogous to the Gibson, Davies, and Ward crystalline polyethylene model in that the regions containing densely packed and oriented PE chains represent the PE crystallites.¹¹³ The regions connecting longitudinally adjacent crystallites consist of amorphous polyethylene, referred to as intra-amorphous phase. These regions comprise entangled polymer molecules and are traversed by crystalline bridges, or the equivalent in Peterlin's model, taut tie molecules.¹¹⁴ In contrast, the inter-

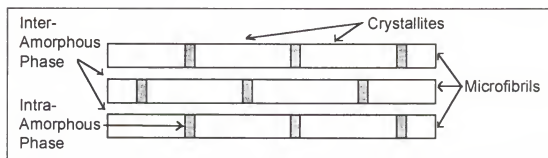


Figure 5-5. A schematic of the microfibrillar morphology of UHMPE fibers.¹¹⁴

amorphous phase most likely contains a much lower concentration of tie molecules between crystallites than the intra-amorphous domains. It is this characteristic that causes UHMPE fibers to fail by fibrillation and exhibit very low shear strengths. However, it is hypothesized that the limiting factor in the mechanical performance of UHMPE fibers is the entanglement density and TTM concentration of the intra-amorphous region.¹¹⁰

It is well known that the long period repeat distance of UHMPE crystallites ranges from 10-25 nm. However, one of the characteristics of UHMPE fibers is an irregular long period. Some long range order is observed for Spectra® 1000 UHMPE fibers but C-NMR on Spectra® 900 fibers reveals a less distinct periodicity.¹¹¹ Using small-angle x-ray scattering (SAXS), Grubb and Prasad observed the same phenomenon for Spectra® 900 fibers and postulated that the irregularity in the long period may be attributed to a partially ordered amorphous domain.¹¹⁶ Data obtained by Wong and Young from Raman spectroscopy demonstrates that there is a bimodal stress distribution in UHMPE fibers upon loading.¹¹⁷ Using a two-phase Takayanagi model to quantitatively assess the modulus of the two phases, it is shown that the modulus of the amorphous phase increases with increasing values of the fiber experimental modulus. Values from 5-20 GPa are obtained for the amorphous-phase modulus. Similarly, Prevorsek *et al.* used WAXD in conjunction with Raman spectroscopy to explain the bimodal strain distribution of UHMPE fibers upon loading.¹¹⁵ Using a hexagonal array crystalline phase model, an amorphous-phase modulus of 1-3 GPa was estimated. Thus, it is evident that although an amorphous phase does exist, the molecules that traverse these regions are not the low-T_g,

rubbery material first anticipated. Rather, the molecules exist in a highly oriented, non-relaxed conformation.

The ramifications of this type of non-equilibrium structure are that, given sufficient energy, the molecules will reorganize. Dijkstra has argued that reorganization, or pullout of the TTMs from adjacent crystallites, will occur when the entropic gain from such an event exceeds the energy needed to slide the chains past one another.¹¹⁰ However, this type of energy balance should also include the enthalpy of fusion to 'melt' any segments of the molecule that are crystallized. It is feasible then that the thermodynamics of the system will drive a redistribution of TTMs upon annealing. An analogous situation occurs when surface energetics are considered. For example, surface modification by gas plasma treatment increases the surface energy of UHMPE fibers through the creation of more polar chemical species at the surface. Provided an opportunity, the low surface energy polyethylene molecules will diffuse to the surface in order to reduce the free energy of the system. Figure 5-6 illustrates this behavior very clearly for air-plasma treated UHMPE fibers.²² As the annealing temperature increases, the mobility of amorphous polyethylene chains increases allowing a greater number to diffuse to the surface and reduce the free energy. If it is these chains that act to bind the crystallites together in UHMPE fibers then the mobility of these chains will drastically affect the overall fiber properties.

There is strong evidence that the failure of UHMPE fibers is initiated by chain scission rather than chain disentanglement or pullout. In addition to showing that a bimodal stress distribution exists upon loading UHMPE fibers, Prevorsek *et al.* also argued that at higher strains decoupling of the crystalline regions occurs via chain scission of the amorphous chains.¹¹⁵ Bastiaansen and Grooters confirm the interpretations of

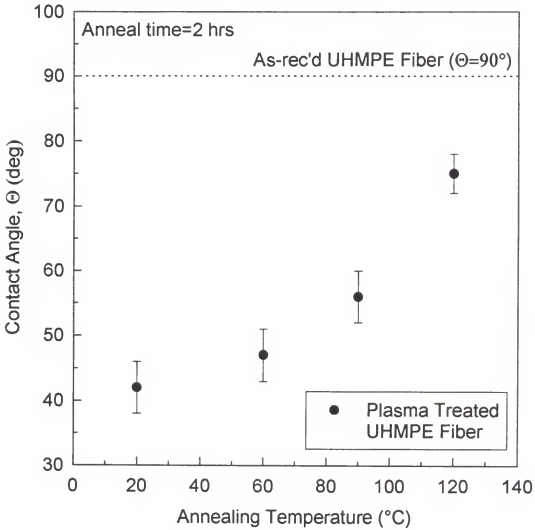


Figure 5-6. Advancing water contact angles of air-plasma treated UHMPE fibers (Spectra® 900) versus annealing temperature (annealing time=2 hrs).²²

Prevorsek *et al.* By copolymerizing propylene with ultra-high molecular weight polyethylene and producing UHMPE fibers using the solution-spinning ultra-drawing process, they showed that the tensile strength of the drawn fibers at a constant modulus is independent of comonomer concentration. Combined with the fact that methyl side groups effectively reduce intermolecular chain slippage, i.e., creep, the data supports the conclusion that the failure process of UHMPE fibers is controlled predominately by chain scission.¹¹⁸ The high resistance to chain slippage is related to the orthorhombic crystal structure. When a crystal phase change to the hexagonal structure occurs, intermolecular chain slippage is less impeded and the strength decreases.¹¹⁹

If chain scission is the controlling factor in the failure process of UHMPE fibers, then the concentration of TTM plays a key role. In fact, Dijkstra and Pennings ascribe the tensile strength of UHMPE fibers to the fraction of load carrying chains, or taut-tie molecules.¹¹⁰ This parameter influences the tensile modulus as well, although the ratio of crystal length to the intra-amorphous domain length apparently plays a more crucial role. It was observed above, that the tensile strength decreased by 68% after annealing near T_m whereas the modulus only exhibited a 25% drop after annealing. Furthermore, DSC and WAXD showed no measurable changes in the crystal/amorphous ratio. Given that the annealing treatment decreases the TTM concentration via a thermodynamic driving force, our observations support the exegesis given by Dijkstra and Pennings that, in contrast to the tensile strength, the TTM concentration does not solely dictate the tensile modulus. Hence, the reduction in TTM caused by annealing dramatically reduces the strength, 68% decrease, but only decreases the tensile modulus by 25%. On the other hand, the

amorphous nature of the TTMs make it more difficult to explain the steadily decreasing trend in the elongation to failure of annealed UHMPE fibers.

Porter and Kanamoto have reviewed the tensile response of polyethylene fibers and highlighted some of the pioneering work in this area.⁴⁶ One area that is yet to be fully explained, is the unusually low elongations to failure, ten-times smaller than the theoretical value estimated from the extension of C-C bonds. Dijkstra and Pennings have postulated that this behavior is the result of a substantially lower energy barrier for the scissioning of entanglements than for the C-C bond.¹¹⁰ Since the intra-amorphous domains contain defects like entanglements, chain ends, twists, etc., it is likely that the scission event is initiated in these regions. Moreover, if the annealing treatment exacerbates any of these defects then a concomitant decrease in elongation to failure will be expected. Considering that prior to annealing the intra-amorphous region consists of highly oriented, non-relaxed polyethylene chains, it seems reasonable that the entanglement density will increase proportionately to the annealing temperature as the chains attain a equilibrium coil-like conformation. The fact that the elongation monotonically decreases with annealing temperature up to 80% supports the predilection of entangling chains.

Fracture Analysis by Scanning Electron Microscopy

UHMPE fibers are characterized by rather low shear strengths and a propensity to rupture by fibrillation due to shear failure. Figure 5-7 shows a typical failure specimen of an as-received UHMPE fiber. The fractured fiber exhibits multiple fragments that appear torn longitudinally down the axis of the fiber. These fragments also reveal a striated texture indicative of the oriented microfibril morphology. Closer inspection of the as-



Figure 5-7. SEM micrograph of as-received UHMPE fiber after tensile failure (magnification x400).

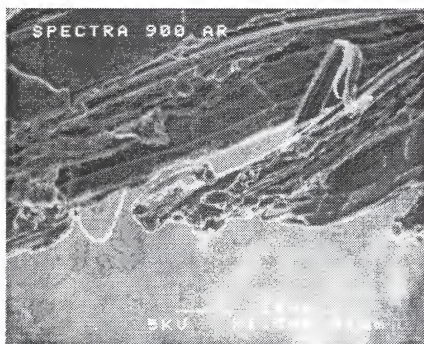


Figure 5-8. SEM micrograph of as-received UHMPE after tensile failure (magnification x1500).

received UHMPE fiber surface, shown in Figure 5-8, reveals a somewhat corrugated surface. The resultant shear forces apparently cause a tearing along multiple fibril surfaces. The fracture surface of the UHMPE fiber annealed at 137°C is shown in Figures 5-9 and 5-10. The fragmentation exhibited by the as-received fibers is absent in the annealed fiber shown in Figure 5-9. Likewise, the shear-induced striations of the as-received fiber are also not prevalent in the annealed fiber. One way to explain the apparent change in fracture mode is through the TTM arguments conjectured hitherto. As described by Dijkstra, the tensile strength of as-received UHMPE fibers is determined by the fraction of load-carrying chains, or TTMs.¹¹⁰ Upon loading an as-received fiber, scission of individual PE chains occurs as the load is increased. Consequently, the applied load is no longer axi-symmetric and shear stresses develop. The resultant shear stresses induce shear failure of the fiber along the inter-amorphous regions between fibrils leaving a fracture surface exemplified by Figures 5-7 and 5-8. On the other hand, the TTM concentration and the corresponding tensile strength decrease following annealing of the UHMPE fiber. Since there are fewer TTMs, chain scission of individual chains is initiated at a lower applied load. Any off-axis stresses that develop are then correspondingly lower and, based on the fracture surfaces of Figures 5-9 and 5-10, are not sufficient to induce considerable shear failure.

Conclusions

The fact that interfacial properties represent the weak link in a composite structure mandates that this area be improved. If composites are to retain their competitive advantage as high strength, lightweight structures and find use in more demanding



Figure 5-9. SEM micrograph of UHMPE fiber annealed at 137°C for 2 hours (magnification x400).

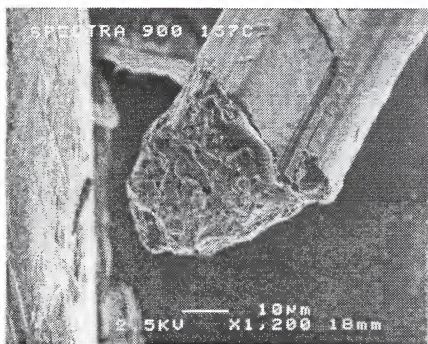


Figure 5-10. SEM micrograph of UHMPE fiber annealed at 137°C for 2 hours (magnification x1200).

applications, then the fiber/matrix adhesion and corresponding off-axis properties must be significantly improved. Moreover, if designers are to begin designing structures with three-phase composites (fiber, matrix, and interphase), then researchers will need to be able to specify interfacial properties with confidence. This necessitates a better recognition of fiber/matrix interactions and the adhesion test employed, as well as the process dependency of the fiber and matrix, if any. This is particularly important in the case of polymeric fibers.

For instance, this chapter demonstrates that a strong temperature dependence exists for UHMPE fibers annealed for two hours at temperatures below the T_m . Simple tensile tests show that the tensile strength begins to decrease notably when annealed above 100°C. Likewise, the tensile modulus exhibits a marked drop when annealed above 130°C. The elongation to failure, on the other hand, decreases monotonically with annealing temperature. When annealed at the onset temperature of melting, the tensile strength and elongation to failure decrease by a total of 68% and 80%, respectively. In contrast, the tensile modulus shows a maximum decrease of only 25% when annealed at $T_{m(\text{onset})}$. Yet, DSC and WAXD do not reveal any bulk changes in the melting temperature, enthalpy of melting or crystal structure of UHMPE fibers, even when annealed at 140°C. It is conjectured that the highly oriented, non-equilibrium taut-tie molecules relax upon annealing. These morphological changes manifest themselves in a reduction in the overall fraction of load carrying TTMs and an increase in the failure-inducing entanglements. The net result is a decrease in the mechanical properties of UHMPE fibers and a transformation of the failure process as observed by SEM.

CHAPTER 6

HYDROPEROXIDE INITIATED GRAFTING OF POLY(STYRENE-STAT-ACRYLONITRILE) ONTO ULTRA-HIGH MODULUS POLYETHYLENE FIBERS

Introduction

UHMPE fibers represent an excellent opportunity to develop novel surface modification techniques because of their very poor adhesion properties. This characteristic is attributed to their low surface energy, smooth topography, and low concentration of polar chemical species present on the surface. As a result, a variety of surface treatments have been devised for PE fibers including rf plasma, chemical oxidation, gamma radiation, UV radiation, and electron beam treatments. Brennan and George have compiled two comprehensive review articles outlining these techniques for UHMPE fibers.^{28, 29} Further developments in the area of polymer surface modification and adhesion have also been recently compiled by Mittal.¹²⁰

The idea of functionalizing the surface of UHMPE fibers has led to the development of several grafting techniques. The premise behind this approach is that surface grafting imparts the desired surface response while retaining the bulk properties of the substrate polymer. Generally, a monomer is chosen that will increase the fiber surface energy and enhance wettability, or a monomer with reactive functional groups that promotes chemical bonding with the matrix material is selected. Note that there are a multitude of oxidative, non-grafting treatments that improve wettability. Some even provide reactive functionality for chemical bonding. However, polymer grafting

represents a novel method to “hyper” treat the surface and exponentially increase the number of desired functionalities through the graft polymerization process.

Table 6-1 provides a list of the different monomers grafted to UHMPE fibers by various means. The most popular grafting method is rf plasma exposure in which two routes of grafting are viable. The first permits grafting by introducing monomer during the plasma treatment.⁵ The second utilizes non-polymer forming gases in the plasma chamber that yield reactive chemical moieties on the fiber surface. These are subsequently used to initiate grafting off of the surface, e.g., by functionalizing with peroxides or anchoring a Ziegler-Natta catalyst followed by olefin polymerization on the fiber surface.^{39, 42} Similarly, radiation processes such as e-beam, UV, and gamma radiation are also used extensively for surface grafting.²⁸ For example, surface grafting of acrylic polymers onto UHMPE fibers is possible using a low dose rate and low total dose gamma radiation surface modification.³³

Table 6-1. Summary of UHMPE fiber surface grafting methods and monomers.

PLASMA	GAMMA	UV-RADIATION	E-BEAM
Acrylamide (Peroxide) ³⁹	Acrylic Acid-HDPE Fibers ⁴⁰	Acrylamide ²⁵	Acrylic Acid ⁴¹
Glycidyl Methacrylate (Peroxide) ³⁹	Butyl Acrylate ³³	Acrylic Acid ²⁵	
Allylamine ⁵	Cyclohexyl Methacrylate ³³		
Ethylene (Ziegler- Natta) ⁴²	Methyl Methacrylate		
	n-Vinyl Pyrrolidone		
	Allyl Alcohol ⁴³		

The drawback of the aforementioned grafting methods is that many of these techniques require or employ a high energy source to initiate graft polymerization. This adverse feature manifests itself in the lack of control afforded during the polymerization process because of the competition between crosslinking and chain scission mechanisms.^{63, 64} Furthermore, the chosen grafted monomers typically contain pendant groups that are reactive with the matrix material, e.g., glycidyl methacrylate, acrylic acid, and allylamine with an epoxy matrix. This type of graft/matrix system results in a highly crosslinked interphase that is difficult to characterize. As a result, most of the studies to date have only offered phenomenological analyses, e.g., assessments of different surface treatments via simple pullout tests. These tests provide a convenient way to measure adhesion but they lack the sophistication to begin to understand the role of the interphase by a more mechanistic approach. Theoretical models can help forecast the effect of the interphase on the mechanical response of the composite as well as predict the conformation of grafted chains in the interphase.^{70, 71, 121} However, experimentation is still necessary to confirm or deny their predictions. With new imaging methods like Tapping ModeTM atomic force microscopy (TMAFM), it is possible to probe grafted chains at the nanoscale and further substantiate the models. Hence, a grafting method is sought that provides more control of the polymerization process, i.e., graft chain linearity, morphology, and chemical composition, in order to systematically evaluate and tailor the interphase region.

The purpose of this work is to report on the hydroperoxide initiated grafting of poly(styrene-*stat*-acrylonitrile) (SAN) onto UHMPE fibers and to evaluate the applicability of this technique towards designing intelligent interphases, i.e. IntelliGrafts.

The characterization techniques include differential scanning calorimetry (DSC), fiber tensile tests, electron spectroscopy for chemical analysis (ESCA), and TMAFM. DSC and fiber tensile tests are used to monitor the effect of the surface treatment on bulk crystallinity and fiber tensile properties. The nitrogen in poly(styrene-*stat*-acrylonitrile) is used as a marker for ESCA analysis in order to verify grafting. Tapping-Mode™ atomic force microscopy is used to image the surface morphology of the UHMPE fibers. A simple 'hard-sphere' model is presented to explain the polymer graft conformation based on the surface morphology as imaged by AFM.

Experimental

Grafting by Hydroperoxide Surface Modification

UHMPE fibers (Spectra® 900) were obtained from Allied Signal, Inc. The fibers, 6 mm long, were first washed in refluxing acetone (Fisher Scientific) at 58°C for 2 hours, followed by an additional wash in benzene (Fisher Scientific) at 70°C for 1.5 hours. After the washing step, the fibers were hydroperoxidized (HPX) and grafted.

The grafting technique is adapted from the work of George and Willis who developed a method of producing hydroperoxide functional groups on the surface of UHMPE fibers.⁷⁴ According to their procedure, the fibers were immersed in an AIBN/Benzene solution (0.05 M) at 70-80°C through which oxygen is vigorously bubbled. Azobisisobutyronitrile (AIBN) (Kodak) was recrystallized three times prior to use. The starting AIBN/Benzene hydroperoxidation solution volume was 100 ml combined with about 0.6 g of UHMPE fibers. An additional 50 ml of AIBN/Benzene solution was added after the first and second hours resulting in a total hydroperoxidation

time of three hours. This ensures that the free radical supply is replenished since the half life of AIBN radicals is approximately 2-4 hrs. at 70°C-75°C.¹²²

Following the hydroperoxidation, the fibers were filtered and placed in a round bottom flask containing styrene and acrylonitrile monomers (3:1 styrene to acrylonitrile weight ratio; total weight equal to 30 g) and toluene (Fisher Scientific) with a monomer concentration equal to 50 wt%. The acrylonitrile monomer was passed through an inhibitor removal column (Aldrich) and kept over molecular sieves, and the styrene (Aldrich) monomer was fractionally distilled (middle 85% used) under vacuum before using. Prior to heating, the flask was purged by bubbling nitrogen gas through the flask for 5 minutes. The grafting reaction was carried out at 70°C for 15 hours under a nitrogen atmosphere. Subsequently, the fibers were washed thoroughly by continually flushing with tetrahydrofuran (THF) (Fisher Scientific) until clean. Aliquots of the THF wash solution were analyzed periodically using a Hewlett Packard UV/VIS spectrometer to detect residual monomer, SAN homopolymer, or toluene. Although the washing step can take 3-5 days, the sensitivity of the UV/VIS spectrometer (to 50 ppm) provides confidence that the fibers were completely free of adsorbed polymer or monomer. After washing, the fibers were dried and analyzed by DSC, ESCA, and tapping-mode atomic force microscopy. This procedure was repeated for 381 mm long UHMPE fibers to provide samples for tensile testing.

Characterization of UHMPE Fibers and SAN Grafts

The thermal response curves of the UHMPE fibers were obtained using a Seiko model DSC 220C (heat-flux type). The DSC was interfaced with a Seiko 5600H Rheostation that was used to collect and assimilate the data. The sample-side

thermocouple and DSC signal were calibrated using indium, tin, and bismuth standards. A heating rate of 10°C/min was utilized, and a dry nitrogen atmosphere was maintained at a flow rate of approximately 100 ml/min. Sample weights were maintained near 10 mg. The enthalpy of melting and peak and onset melting temperatures were quantified using the thermal analysis software.

Fiber tensile properties were measured using an Instron 1122 mechanical tester with an 890 Newton load cell. Single UHMPE fibers were tested according to ASTM D2256 at a rate of 100%/min and a gage length of 254 mm. An average fiber diameter of 38 μm was calculated based on the fiber denier of 650 and 60 fibers per bundle.

ESCA was performed on a Kratos DS800 spectrometer (spectral resolution of 1.1 eV) using $\text{MgK}\alpha$ incident radiation (1.2536 keV). Short (6 mm) fibers were washed in ethanol, dried at 50°C, carefully secured to steel mounts using double sided tape, and analyzed. The highlighted spectra represent scans through the region characterized by an ejected N1s orbital electron (399 eV). Scans in the regions corresponding with an ejected C1s and O1s orbital electron were also collected as well as survey scans, but are not shown. The survey scans revealed trace amounts of silicon present in each of the fibers.

Tapping-mode atomic force microscopy (TMAFM) was conducted using a Nanoscope® III (Digital Instruments, Santa Barbara, CA) instrument. Images (1 μm x 1 μm) were collected at a scan rate of 1.5 Hz and a vertical tip oscillation frequency ca. 350 kHz. Single crystal silicon cantilever tips (radius of tip=5-10 nm) with a spring constant of 20-100 N/m were used. An operation setpoint equal to approximately 75% of the undamped free oscillation amplitude of the tip was chosen. Higher setpoint voltages correspond with lower contact forces.

Results and Discussion

Thermal and Mechanical Properties of UHMPE Fibers

One of the drawbacks of conventional surface treatments is the adverse effect these schemes have on the fiber tensile properties. For example, a commercial plasma treatment of UHMPE fibers leads to a 10% reduction in the tensile strength.¹ Thus, an objective in this research was to develop surface modification routes that minimize this type of damage.

Using chemiluminescence, George and Willis showed that the peroxide concentration of hydroperoxidized UHMPE fibers increased monotonically with peroxidation time up to 3 hours.⁷⁴ However, it was also shown that hydroperoxidation of UHMPE fibers for 3 hours led to a 10% decrease in the fiber tensile strength. The mechanism for chemiluminescence from the thermolysis of hydroperoxides has been attributed to a bimolecular reaction between alkyl peroxy radicals produced by abstraction of the hydrogen atom from hydroperoxides by the mobile hydroxy radical.²⁹ This termination reaction produces an alcohol, singlet oxygen and an excited carbonyl group. Since the formation of carbonyl species along the polyethylene molecular backbone inherently leads to chain scission, a decrease in strength is anticipated following extensive hydroperoxidation and thermolysis in the presence of oxygen. This might suggest the use of shorter peroxidation times. Nevertheless, a hydroperoxidation time of three hours was chosen to obtain the maximum concentration of grafting sites. Besides, the grafting process should consume the hydroperoxides, thus mitigating the deleterious effects of

surface oxidation and chain scission. In order to determine the effect of this additional time on the fibers, thermal and mechanical properties were characterized.

The tensile properties of the UHMPE fibers are summarized in Table 6-2. "Washed" denotes the effect of washing the fibers in refluxing acetone for 2 hours and in benzene at 70°C for 1.5 hours. As-received, "washed," hydroperoxidized, and SAN-grafted fibers were viewed under an optical microscope to see if changes in fiber diameter had occurred upon treatment. Based on these observations, the fiber diameter did not appear to change, and it appeared that the calculated diameter of 38 μm more accurately represented the minimum fiber diameter. The tensile properties are graphically represented in Figure 6-1. A comparison between the elastic moduli shows very little difference. However, both the elongation-to-failure and the tensile strength decrease slightly after washing and progressing through the treatment process. The largest decrease is exhibited by the HPX sample. Although the averages of the as-received and HPX fibers are not significantly different ($\alpha=0.05$), it was evident when testing the HPX fibers that certain fibers in the set were more strongly affected than others. These fibers were characterized by a more brittle response with a tensile strength near 1.3 GPa and an elongation-to-failure of 1.8%. Interestingly, the SAN-grafted fibers did not reveal this same response as evidenced by the reduction in the standard deviation back to its original level. This result supports our postulate that the grafting reaction mitigates carbonyl group formation and the adverse effects associated with chain scission.

DSC was used to evaluate the effect of grafting on the crystallinity. Table 6-3 lists the enthalpy of melting for the as-received, hydroperoxidized, and SAN-grafted

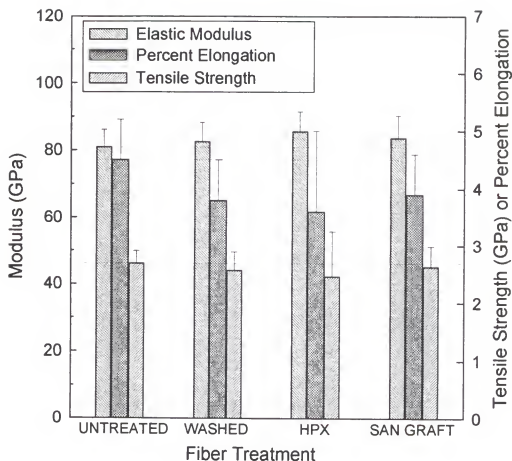


Figure 6-1. Tensile properties of UHMPE single filaments (ASTM D2256). "Washed" denotes cleaned in refluxing acetone for 2 hr. and benzene at 70°C for 1.5 hr. The horizontal reference lines denote the average properties of the as-received fibers. The error bars represent one standard deviation of the sample distribution (6-9 samples tested per group).

Table 6-2. Tensile Properties of UHMPE Single Fibers.

<i>UHMPE Fiber</i>	Modulus (GPa)	Tensile Strength (GPa)	Elongation (%)
As-received	80.9 ± 5.2	2.69 ± 0.22	4.5 ± 0.7
Washed	82.5 ± 5.8	2.57 ± 0.32	3.8 ± 0.7
HPX	85.5 ± 6.0	2.46 ± 0.79	3.6 ± 1.4
SAN-grafted	83.6 ± 6.7	2.63 ± 0.36	3.9 ± 0.7

*Values represent the average and standard deviation of 6-9 samples.

Table 6-3. Enthalpy of melting (J/g) for UHMPE fibers.

As-received	Hydroperoxidized (3 hrs.)	SAN-grafted
245.4 ± 12.6	258.2	258.9

UHMPE fibers. Based on the literature value for the enthalpy of melting (292.9 J/g), the percent crystallinity of the as-received fibers ranges from 79%-88%.¹²³ The DSC response curves are shown in Figure 6-2. Although there appears to be an upward trend in the enthalpy with treatment, the results are not significant ($\alpha=0.05$) based on the standard deviation obtained from repeated measurements on the UHMPE fibers (see standard deviation of as-received fiber). Thus, no significant changes in the bulk crystalline content have occurred after the hydroperoxidation and grafting steps.

Surface Analysis of the UHMPE Fibers by ESCA

The ESCA analysis of the as-received, hydroperoxidized and SAN-grafted UHMPE fibers are shown in Figures 6-3, 6-4 and 6-5. A peak at a binding energy equal to 399 eV is characteristic of the ejected N1s orbital electron. As expected, the N1s

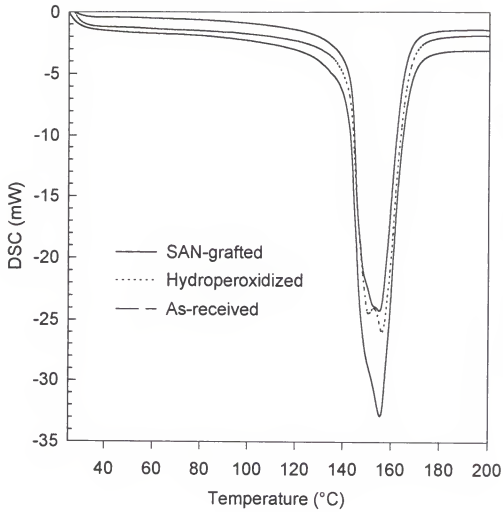


Figure 6-2. DSC response curves of SAN-grafted (top curve), HPX-only (middle curve) and as-received (bottom curve) UHMPE fibers. The difference in the enthalpy of melting after the hydroperoxidation and grafting is not statistically significant.

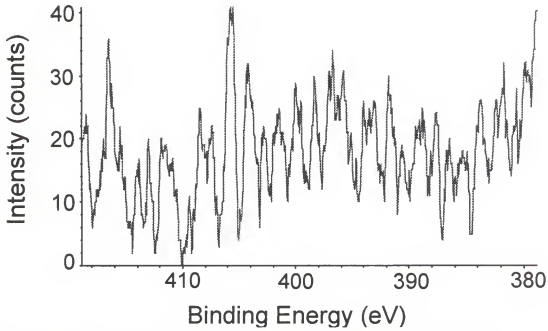


Figure 6-3. High resolution ESCA-N(1s) spectrum of as-received UHMPE fibers.

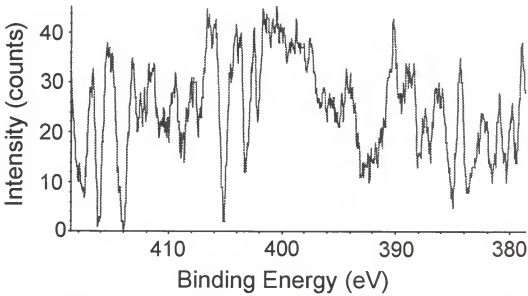


Figure 6-4. High resolution ESCA-N(1s) spectrum of hydroperoxidized UHMPE fibers.

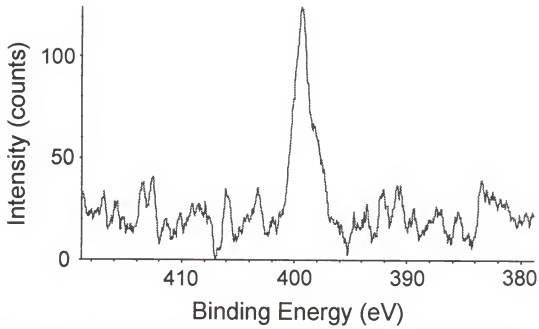


Figure 6-5. High resolution ESCA-N(1s) spectrum of SAN-grafted UHMPE fibers.

scans for the as-received and hydroperoxidized UHMPE fibers do not reveal nitrogen at levels above the detectable limit. However, it is clear that the SAN-grafted fiber contains nitrogen indicating that the SAN copolymer was successfully grafted. The quantitative ESCA results are shown in Table 6-4 and indicate that the SAN-grafted fibers comprise 2.3 atomic percent nitrogen. Since the graft polymerization was performed at the azeotropic composition of styrene and acrylonitrile, the anticipated graft composition is equal to the feed composition (3:1 styrene to acrylonitrile by weight). SAN at its azeotropic composition contains 6.2 atomic percent nitrogen. However, ESCA analysis of the SAN homopolymer extracted from the grafting solution shows a nitrogen content of 2.5 atomic percent. Based on this analysis, a 92% coverage is achieved by hydroperoxidation induced grafting. Quantifying the extent of grafting by weight gain measurements is impractical because of the predominance of surface grafting. For example, a polymer layer, 30 nm thick, grafted with 100% coverage yields a weight gain only on the order of 0.3 %.

Table 6-4. Quantitative ESCA analysis of UHMPE Fibers.

<i>Material</i>	Atomic Concentration (%)		
	Carbon	Oxygen	Nitrogen
UHMPE Fiber:			
As-received	89.3	10.7	—
HPX	80.6	19.4	—
SAN-grafted	90.4	7.3	2.3
SAN	93.6	3.9	2.5
homopolymer			

The quantitative ESCA results (Table 6-4) also show the effect of hydroperoxidation on the surface oxygen concentration. After the hydroperoxidation

treatment the oxygen content nearly doubles because of the formation of oxidative species. Based on attenuated total reflectance (ATR) FTIR of hydroperoxidized HDPE films (ATR/FTIR analysis of SAN-grafted UHMPE fibers was unable to detect the graft polymer), the increased oxygen concentration is associated with carbonyl and alcohol functional groups. However, the IR absorption corresponding to alkyl peroxides is not observed, probably because the peroxides thermally decompose during storage. As mentioned previously, the thermolysis of hydroperoxides produces both alcohol and carbonyl groups.²⁹ Further examination of the quantitative ESCA results shows that the oxygen content of the SAN-grafted fibers decreases to below that of the as-received UHMPE fibers. This result is corroborated by the ATR/FTIR of HDPE mentioned above, in that the IR absorptions associated with the oxidative species decrease in relative intensity following the grafting. This result further supports our postulate that grafting consumes the hydroperoxides and precludes the formation of oxidative species. Austin *et al.* further substantiated these findings using ESCA and a dye assay to show that allyl alcohol was preferentially grafted on the surface, rather than through the bulk, of UHMPE fibers (Spectra® 1000, Allied Signal).⁴³ Thus, the SAN grafts are initiated by the thermolysis of hydroperoxides, propagate by a free radical mechanism and based on ESCA analysis, are preferentially surface grafted.

Atomic Force Microscopy of UHMPE Fibers

The TMAFM image of the as-received UHMPE fiber is shown in Figure 6-6. The image shows the fibrillar morphology and the orientation of the macrofibrils along the fiber longitudinal axis (oriented from the lower left to the upper right hand corners of the

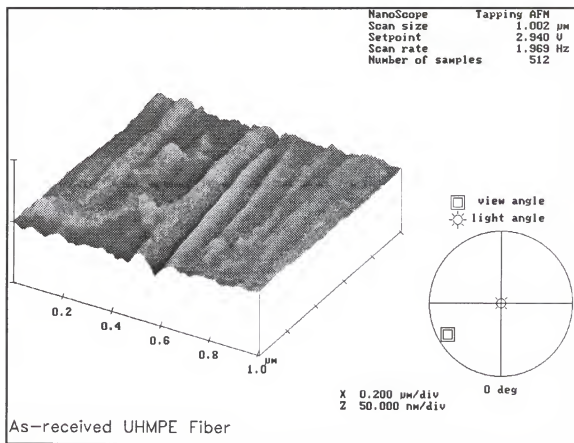


Figure 6-6. TMAFM™ images of as-received UHMPE fiber. Macrofibrils are 50 nm wide and 15-20 nm in height.

image). The macrofibrils represent one of the structural elements that comprise the hierarchical morphology of polyethylene. The macrofibrils seen here are approximately 50 nm in diameter and 15-20 nm in height. The macrofibrils are actually composed of microfibrils, the main building blocks of the hierarchical structure, which are 2-7 nm in width.¹¹¹ The surface topography of the hydroperoxidized UHMPE fiber is not shown since it closely resembles the as-received morphology.

The surface of the SAN-grafted UHMPE fiber is shown in Figure 6-7. The SAN-grafted fiber exhibits a highly textured surface topography comprised of uniformly distributed SAN graft polymer in the form of nodules. On close examination of the SAN-grafted surface, it is still possible to see the fibrillar morphology below the surface of the SAN nodules. The SAN nodules vary in size from 3-12 nm in height and are 10-25 nm apart. The dimensions of the grafted layer seen here are consistent with the work of Zhang *et al.* where the depth (10-15 nm) of a poly(acrylic acid) grafted layer on Kevlar®49 was determined by Ar⁺ etching and ESCA analysis.⁴⁵ The questions that were asked included, "What do the nodules represent? Could they represent individual polymer chains adopting a random coil-like conformation?" The following discussion will provide one possible explanation and a simple model to support our hypotheses.

After the hydroperoxidation treatment, the fiber surface was functionalized with hydroperoxide groups. During the grafting reaction, the hydroperoxides thermally decompose and two radicals are formed. The radical remaining attached to the surface of the UHMPE fiber is subsequently able to initiate a free radical polymerization. The work described here involves the hydroperoxide initiated grafting of a styrene/acrylonitrile

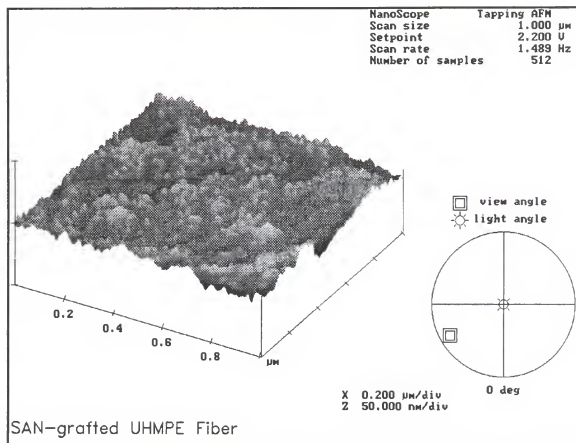


Figure 6-7. TMAFMTM images of SAN-grafted UHMPE fiber. The textured surface is composed of nodules, 3-12 nm wide and 10-25 nm apart.

copolymer at its azeotropic composition. Light scattering experiments done on separate free radically polymerized styrene/acrylonitrile show that this polymer system formed linear chains with negligible branching. Thus, the same was expected of the grafting polymerization. This aspect of the hydroperoxidation grafting is attractive since the hydrodynamics of linear chains is better understood and can be related to the surface morphology of the fibers as imaged by atomic force microscopy.

It is well known that the long period repeat distance of UHMPE crystallites ranges from 10-20 nm. This result is confirmed by both small angle x-ray scattering of UHMPE films and high resolution, liquid-cell AFM of UHMPE (Spectra® 900) fibers.^{111, 113} If the Gibson, Davies, and Ward model for the structure of the crystalline polyethylene is invoked, the top surface of the UHMPE fiber can be represented as shown in Figure 6-8.¹¹³ The thin horizontal lines represent fully extended polyethylene chains, or microfibrils as proposed by Peterlin, oriented along the fiber axis.¹¹⁴ The regions containing densely packed and oriented PE chains represent the PE crystallites with an associated long period repeat distance, L . The lines joining adjacent crystallites denote a crystalline bridge. These are also referred to as taut tie molecules according to Peterlin's model. The blank regions between the crystallites, traversed by taut tie molecules, represent the amorphous domains. As expected, the surface structure of the substrate has direct ramifications on the graft morphology.

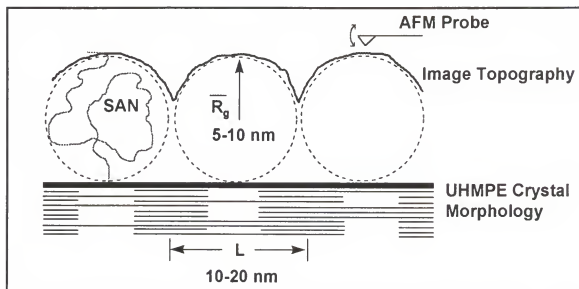


Figure 6-8. 'Hard-Sphere' model of the SAN graft conformation on the surface of UHMPE fibers. The thin horizontal lines represent fully extended polyethylene chains, or microfibrils as proposed by Peterlin, oriented along the fiber axis.¹¹⁴ The regions containing densely packed and oriented PE chains represent the PE crystallites with an associated long period repeat distance, L . The lines joining adjacent crystallites denote a crystalline bridge. These are also referred to as taut tie molecules according to Peterlin's model.¹¹⁴ The blank regions between the crystallites, traversed by taut tie molecules, represent the amorphous domains. The SAN grafts are tethered from the amorphous surface domains and assume a random coil conformation, represented as 'hard spheres'.

Austin *et al.* used ESR studies to show that irradiated polyethylene forms free radicals in both the amorphous and crystalline regimes.⁴³ However, the allyl alcohol monomer is only able to diffuse through the amorphous polymer, and as a result, the free radicals in the crystalline domains are not consumed during the grafting reaction. Hence, the grafting reaction predominates in the amorphous regime. The same behavior is expected for the hydroperoxidized UHMPE fibers. If grafting is isolated to amorphous domains, then the SAN grafts will be distributed according to the spacing of amorphous regions along the fiber surface. In other words, the graft spacing will correlate directly with the long period repeat distance of the UHMPE crystallites. This understanding of the UHMPE crystal morphology and grafting mechanism will help elucidate the atomic force microscope images.

As shown in Figure 6-8, the SAN grafts are represented by a chain tethered from an amorphous region along the surface. If the grafted polymer assumes a random coil conformation, the polymer is, in turn, represented as a hard sphere resting on the surface of the fiber. And if a single chain is grafted from each amorphous segment of the UHMPE surface, the resulting hard spheres will lie on the surface and will each have an associated radius equal to the radius of gyration of the grafted polymer. Given that the long period repeat distance of UHMPE fibers is 10-20 nm, the radius of the polymer spheres at which the spheres just begin to impinge is equal to 5-10 nm. Interestingly, both the nodule spacing (10-25 nm) and the nodule height range (3-12 nm) are consistent with the scenario depicted in Figure 6-8. Accordingly, the grafted SAN spheres do begin to impinge. The implication of this type of close packing on the AFM analysis is that the probe tip will image only the tops of the spheres as indicated by the dark line in Figure 6-8. The

resulting image will comprise spherical nodules, with only the top half discernible and the height equal to the radius of gyration of the underlying sphere.

If a cross section of Figure 6-7 is taken so that the fiber surface is observed in the x-z plane only, a distribution of nodule heights is obtained. The resulting image topography is analogous to the dark line traced by the AFM probe depicted in Figure 6-8. According to the discussions above, the height of each nodule is a measure of the radius of gyration of the grafted polymer chain and the radius of gyration is related to the mean end-to-end distance according to simple random coil statistics. The governing equations for this analysis are shown in Figure 6-9.¹²⁴ One modification is made to the random coil mean end-to-end distance for the tethered chain. Since the SAN graft is tethered to an impenetrable surface, a factor of 2 is introduced to correct for the probability that a chain end can be found between 0 and ∞ , rather than between $-\infty$ and ∞ . Thus, a tethered chain with the same molar mass as a free chain will have twice the mean end-to-end distance as the free chain.

If the bond angle and rotation angle restrictions of polystyrene are substituted into the equation for a tethered graft, a measure of the graft molar mass distribution (MMD) is obtained. The results are shown in Table 6-5. The MMD of the SAN homopolymer was measured by gel permeation chromatography (GPC) (Waters) according to calibrations using polystyrene standards. It is evident that the molar masses computed from the AFM images differ significantly from the measured values for the homopolymer. However, there are several contributing factors to this discrepancy. First, the problem of using a linear section analysis to obtain a height distribution inherently yields values on the low side. Since it is impossible to take a linear slice that bisects each nodule perfectly, the

Free Polymer Chain

$$\langle r^2 \rangle = n l^2 \left(\frac{1 - \langle \cos \Theta \rangle}{1 + \langle \cos \Theta \rangle} \right) \left(\frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \right)$$

$$\langle r_g^2 \rangle = \frac{1}{6} \langle r^2 \rangle$$

Polymer Tethered to Impenetrable Surface

$$\langle r^2 \rangle = 2n l^2 \left(\frac{1 - \langle \cos \Theta \rangle}{1 + \langle \cos \Theta \rangle} \right) \left(\frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \right)$$

Bond Angle Characteristics of Polystyrene

$$\Theta = 109.5^\circ \quad \left(\frac{1 + \langle \cos \Phi \rangle}{1 - \langle \cos \Phi \rangle} \right)^{1/2} = 2.44$$

Molecular Weight Calculation

$$\text{MW} = \frac{n}{2} (0.75 M_S + 0.25 M_{AN})$$

Figure 6-9. Root mean square end-to-end distance of a free and a tethered polymer chain with corresponding equations for the determination of the radius of gyration and the polymer molar mass. The mean end-to-end distance, r , is expressed in terms of the degree of polymerization, n , the backbone bond length, l , and the fixed bond angle and bond rotation restrictions, θ and Φ , respectively. The mean end-to-end distance is related to the radius of gyration, r_g , by a factor of six. M_S and M_{AN} represent the molar mass of styrene and acrylonitrile, respectively.

height values will not always represent the radius of gyration. Our arguments also err on the low side since chain statistics (bond angle and rotation angle restrictions for polystyrene at theta conditions) that apply for polymers in solution under theta conditions were applied. Initially, this presented a major obstacle to overcome but new liquid-cell tapping-mode AFM techniques will allow us to look at grafted surfaces in various solvents. It is also possible that the average molar mass of the grafts is lower than the molar mass of the homopolymer. Since the grafts are tethered to a bulky fiber, the growing polymer chain is more constrained than under typical solution polymerization conditions. Consequently, monomer/chain end collisions are limited because the monomer must diffuse to the fiber surface and find the chain end. Since the grafts adopt a coil conformation, it is also possible that a cage-effect limits the accessibility of the chain end causing a corresponding ceiling in the molar mass. This type of analysis would explain the observed lower polydispersity index of the SAN grafts relative to the homopolymer.

Table 6-5. Molar mass distribution of SAN homopolymer and predictions of SAN grafts based on AFM.

SAN (3:1)	$\langle r_g \rangle$ (nm)	Mn (kg/mol)	Mw (kg/mol)	Mw/Mn
Homopolymer	12.6 (calc.)	176	364	2.1
Non-Tethered Grafts	7.1 (AFM)	52	67	1.3
Tethered Grafts	7.1 (AFM)	26	33.5	1.3

It should also be pointed out that several assumptions were made regarding the surface crystalline morphology of the UHMPE fibers. Although DSC showed no significant changes in the bulk crystallinity, it is possible that the surface morphology is changed following hydroperoxidation. Since the hard sphere model is based on this morphology, any changes would have direct repercussions on this type of analysis. Based on ATR/FTIR, ESCA and tensile test characterization, the grafting reaction does mitigate the deleterious effects of surface oxidation and chain scission associated with the thermolysis of hydroperoxides. However, it is still possible that some reorganization and/or damage of surface regions occurs following grafting, even if the grafting is confined to the amorphous domains only. Perhaps this explains the discrepancy between the nodule spacings (10-25 nm) and the long period (10-20 nm) of UHMPE crystallites. The identification of the precise surface variations would benefit from an experimental determination of the surface crystallinity, e.g., by glancing angle x-ray diffraction, and would provide an experimental basis for the determination of the graft anchoring density and graft molar mass, both highly relevant for technological applications.

Conclusions

A new approach has been developed regarding the surface modification of high performance UHMPE fibers for advanced composites. Our approach is to engineer intelligent interphases using a hydroperoxide initiated grafting technique that provides a novel method of grafting by a free radical-type polymerization. This approach is attractive over some of the more conventional surface grafting methods because it is not deleterious to the fiber mechanical properties. Surface analysis of the poly(styrene-*stat*-

acrylonitrile)-grafted UHMPE fibers was performed using ESCA and TMAFM. The nitrogen in the SAN was used as a marker to verify grafting by ESCA. Quantitative ESCA and FTIR analyses revealed that the grafts were preferentially surface-grafted, rather than bulk-grafted. The surface topography of the SAN-grafted UHMPE fiber was imaged by TMAFM and showed a distinct topography comprised of nodules, 3-12 nm in height and 10-25 nm apart. A 'hard-sphere' model was developed based on the crystalline morphology of polyethylene and simple random coil statistics of polymer chains. The modeling corroborates our hypothesis that the nodules represent individual linear chain grafts that are tethered in the amorphous regime of the polyethylene substrate. Thus, a method has been developed for analyzing the morphology of the polymeric grafts, correlating this structure with the graft molar mass, and relating these results to the graft behavior at the surface and in the interphase. It is now possible to explore different aspects of surface grafting such as the effect of molar mass and chain stiffness using more advanced scanning probe techniques, and ultimately, further elucidate the role of the interphase in composites.

CHAPTER 7

TAILORED COMPOSITE RESPONSE THROUGH FIBER SURFACE GRAFTING

Introduction

As composites support a broader array of structural applications for surface transportation, commercial aircraft, and public works, the demands on these materials will become even more stringent. The rigorous conditions to which these materials will be exposed require that they withstand complex stress conditions and yet maintain their competitive advantage of high specific strength and exhibit impact resistance. Both of these properties are strongly dependent on the fiber/matrix adhesion. However, the lack of mutual exclusivity between fiber/matrix adhesion and toughness has led to different strategies for improvements in these areas.

Under tensile loading conditions in which the stress is oriented parallel to the fiber axis, increased fiber/matrix adhesion promotes better stress transfer from the matrix to the fiber, providing more efficient mechanical reinforcement. When off-axis stresses develop, the fiber/matrix adhesion plays an even greater role because of the larger shear stresses that are generated. Table 7-1 lists the ranges of interlaminar shear strength (ILSS) values of some typical high performance fibers.⁵ In the case of carbon and glass fibers these values are not quite as deficient as those for the high performance polymeric fibers. For instance, if the matrix polymer has a tensile yield strength of 50-100 MPa, then the matrix shear strength computed according to the von Mises criterion ($\sigma_s = \sigma_y/3^{1/2}$) is 29-58 MPa.

According to this scenario, the interfacial shear strength of the polymeric fibers falls below the matrix shear strength. Thus, the interfacial properties represent the weak link in a composite structure and consequently, the majority of composite failures involve interfacial debonding.⁶ If composites are to retain their competitive advantage as high strength, lightweight structures and find use in applications that are more demanding, then the fiber/matrix adhesion and corresponding off-axis properties must be significantly improved. Consequently, considerable effort has been focused on improvements in this area, in particular, for ultra-high modulus polyethylene (UHMPE) fibers.

Table 7-1. ILSS Ranges of Typical High Performance Fibers.

<i>Fiber</i>	UHMPE	Aramid	Carbon	Glass
ILSS (MPa)	8-17	21-40	66-110	55-97

Off-axis properties such as shear and transverse strength are generally increased with improved fiber/matrix adhesion. Likewise, the longitudinal properties of fiber-reinforced composites are maximized through conditions of good fiber/matrix adhesion and the accompanying efficient transfer of stress from the matrix to the fiber. The mechanisms for adhesion are trifurcated into (i) chemical bonding, (ii) mechanical interlocking and (iii) physicochemical bonding. Generally, the improved adhesion is achieved through oxidative surface treatments, e.g., plasma exposure, that either functionalize the surface with reactive chemical groups, increase the surface energy and hence the wettability, and/or roughen the surface to promote mechanical interlocking between the fiber and matrix. However, this approach tends to improve adhesion to the extent that fiber debonding and pullout during fracture are inhibited. The result is

diminished impact resistance. Consequently, impact properties of fiber reinforced composites are optimized by a different approach.

It is recognized that a strong fiber/matrix bond is deleterious to the impact and damage tolerance properties of composites, and, in fact, conclusive evidence of this result exists for nearly all of the high-performance reinforcing fibers.^{4, 6, 17} When impact toughness is at a premium, surface treatments that reduce the interfacial strength are employed.⁵⁰ Thus, additional energy is absorbed through the Cook-Gordon mechanism in which the triaxial stress state ahead of the crack tip causes fiber/matrix debonding.⁵¹ This failure mechanism effectively blunts the propagating crack and makes the crack path more tortuous. In this regard, research efforts have focused on fiber surface treatments that promote this mode of failure and thus increase the energy dissipating capacity of composite structures.⁵⁰

The concept of improving the composite toughness by employing weak, rubbery interfacial layers was first introduced by Broutman and Agarwal.⁵⁴ Using finite element analysis, they showed that a low modulus interphase could improve the energy absorbing capability of the composite. Since then, the most popular method of attaining maximum toughness in fiber-reinforced composites involves the grafting, coating, or depositing of weak, rubbery ($E < 100$ MPa) interlayers.^{50, 60, 61, 68} With the exception of a few examples, most studies employing this technique show a decrease in the interfacial shear strength upon the application of a rubbery interphase. Pittman *et al.* have achieved a 150% increase in the impact strength of low-modulus, polyurethane-grafted carbon fibers with no loss in the ILSS.⁶⁸ Similarly, Crasto *et al.* showed a 63% improvement in the

ILSS of 80:20 poly(ethylene-*stat*-acrylic acid) electrocoated carbon fibers with a modest 15% increase in the impact strength.⁶¹ The inherent drawback of the latter approach is that coatings are susceptible to forced removal under rigorous processing conditions. And depending on the miscibility of the coating with the matrix, the ability of the coating to perform as an effective interphase may be reduced. Moreover, the absence of a chemical bond between the fiber and the interphase material may sacrifice mechanical integrity. For example, a quarter model finite element analysis shows that the shear stress is at a maximum at the fiber/interphase interface.^{58, 125} This result highlights the importance of attaining an interphase that is chemically bonded to the fiber in order to maximize the shear strength at the fiber/interphase margin.

Thus, a truly synergistic interphase has yet to be achieved because the use of grafted polymers at the interphase that are sufficiently stiff ($E > 100$ MPa) to allow adequate stress transfer between the fiber and matrix, and ductile enough to provide mechanisms for energy dissipation, has largely been overlooked. This leads us to the first objective of this section: to study interphases that are chemically grafted to the fiber using the hydroperoxidation grafting procedure (Chapter 6).

There is evidence from shear lag theory modeling experiments that a ductile interphase with a modulus less than that of the matrix might provide synergy between stress transfer levels and energy dissipation. The shear lag analysis was first proposed by Cox *et al.* to derive the fiber stress distribution along the length of a discontinuous fiber.¹²⁶ It is a useful model because it yields the stress transfer characteristics at the fiber/matrix interface. One of the assumptions of the shear lag approach is that the fiber/matrix adhesion is ideal. If, for example, the interphase modulus is varied in the

model, the level of adhesion is assumed to remain unchanged. Although the shear lag analysis is intended for short fibers, the principle upon which it is based involves the mechanics of stress transfer between the fiber and matrix. This principle allows us to model the effect of the interphase modulus on the stress transfer characteristics.

Tsai *et al.* first included a third phase, i.e., interphase, in the elastic shear lag analysis of micro-indentation experiments to determine the material properties of the interphase.¹²¹ Figure 7-1 shows a cross-section and free body diagram of the composite including the interphase region. The radii of each of the constituents is indicated in the cross-section in which the subscripts f, m, and i represent the fiber, matrix, and interphase, respectively. The free body diagram in the lower portion of the figure represents an infinitesimal slice with length, dz . The thickness of the interphase is indicated by t_i , the tensile force as F , and the shear stress as τ . It is assumed in the model that the interphase consists of a cylindrical shell around the fiber with constant thickness. This assumption is partly invalid since homogeneous surface grafting and a monodisperse molar mass distribution are required to satisfy this condition. The latter is especially unrealistic with an addition-polymerized graft copolymer. However, the upper and lower limits of the interphase modulus can be extracted from the model, which will be used to select appropriate graft polymer compositions and engineer an interphase.

Prior to solving the equilibrium equations from the free body diagram, several assumptions are made. First, the constituents are presumed to be linearly elastic under the applied strain. At low strains the epoxy matrix and UHMPE fibers satisfy this requirement. An additional assumption is that the interphase and matrix support both

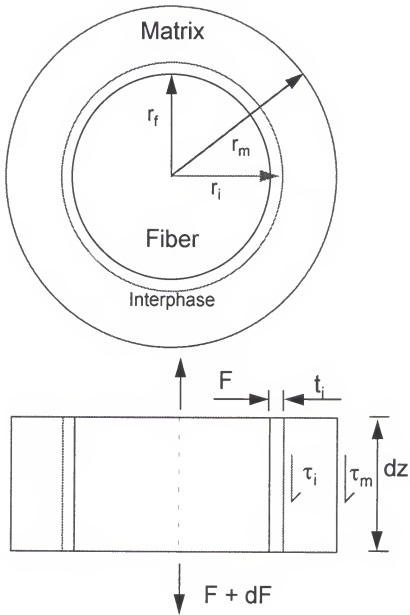


Figure 7-1. Schematic of cross section (top portion) and free body diagram (bottom portion) of composite with interphase.

tensile and shear stresses and that the tensile stress is constant. The fiber supports only tensile loads. When the tensile stress is constant in the interphase and matrix, the product of the radius and shear stress is constant anywhere along the cross section such that $r_i \tau_i = r_f \tau_f = r_m \tau_m$. This result is consistent with the work of Di Anselmo *et al.* who showed that the shear stress at the fiber/interphase margin exceeds that at the interphase/matrix interface.¹²⁷

Consequently, the equilibrium shear stress distributions for the case of a composite without an interphase may be expressed as follows:

$$\tau_f(z) = \frac{\beta \epsilon E_f r_f}{2} \left(1 - \frac{\sinh(\beta z / r_f)}{\cosh(\beta l_f / 2 r_f)} \right)$$

where

$$\beta = \sqrt{\frac{2G_m}{E_f r_f^2 \ln\left(\frac{r_m}{r_f}\right)}}$$

and ϵ is equal to the applied strain, E the Young's modulus, l the fiber length, and G the shear modulus.¹²⁶ Likewise the equation for the composite with an interphase is expressed as follows:

$$\tau_f(z) = \alpha E_f \epsilon \left(\frac{G_m}{2E_f} \right)^{1/2} \left(\frac{\sinh(\alpha z / r_f)}{\cosh(\alpha l_f / 2 r_f)} \right)$$

where

Note that the interphase thickness is equal to $(r_i - r_f)$.¹²¹ Note also that the boundary condition, $\sigma_f(z=0, l_f) = 0$ is satisfied. In other words, the fiber stress at the fiber ends increases from zero at a rate depending on the stress transfer efficiency, up to a maximum at half the fiber length. The shear stress at any point along the length of the fiber is expressed as

$$\tau(z) = \frac{d\sigma}{dz}$$

Thus, the shear stress is equal to the rate of stress transfer from the matrix or interphase to the fiber. A higher stress gradient is indicative of better stress transfer between the fiber and matrix, but also signifies a higher shear stress at the interphase that may lead to debonding at the fiber ends and brittle failure if the matrix and interphase materials are brittle. If the material surrounding the fiber is compliant the stress transfer is diminished and a large portion of the fiber is required to transfer stress back into the fiber. Although this portion is rendered ineffective since it doesn't contribute considerably to the reinforcement of the composite, the weak interphase prevents brittle failure.¹²⁸ Hence, a compromise between these two extremes is desired. An interphase that is sufficiently stiff to allow stress transfer, yet ductile enough to fail non-catastrophically at a critical stress (yield stress of interphase polymer) is deemed ideal. Thus, the shear stress parameter can be used to predict the effect of the interphase modulus on the stress transfer characteristics of grafted interphases and demonstrate the feasibility of our approach.

The purpose of this work is to report the effect of a designed interphase on the composite response and to substantiate the concept of a tailorable composite response through fiber surface grafting. A polymeric interphase was chemically grafted onto the surface of ultra-high modulus polyethylene fibers by the hydroperoxidation technique described in chapter 6. The effect of interphase modulus was evaluated by varying the composition of the poly(styrene-*stat*-acrylonitrile-*stat*-butyl acrylate) grafts. In particular, three interphases, each with a different mechanical response were evaluated. In addition, the effect of grafting efficiency, hence the graft attachment density, was studied by changing the hydroperoxidation temperature from 70°C to 50°C.

The copolymer chemical composition was determined using elemental analysis. DSC was used to monitor the T_g of the copolymers, and tensile tests were used to characterize the mechanical properties of the interphase copolymers. Electron spectroscopy for chemical analysis (ESCA) was used to assess the surface compositions of the copolymers and grafted UHMPE fiber surfaces. The composites were characterized using DSC and density measurements to quantify the volume fraction of fibers and the void content. The mechanical properties were determined by the short beam shear test to measure the interlaminar shear strength (ILSS), composite flexural tests and modified Izod impact tests of woven, bidirectional fiber-reinforced, amine-cured epoxy matrix composites.

Experimental

Materials

Plain-woven UHMPE fibers (Spectra[®] 900, Type 903, 0.153 g/in², 21x21, 1200 Denier) were generously supplied by Fiber Materials, Inc. (Biddeford, Maine) and washed and hydroperoxidized according to the procedure outlined in Chapter 6. Azobisisobutyronitrile (AIBN) (Aldrich) was recrystallized in ethanol at 30°C prior to use. The acrylonitrile and butyl acrylate (Aldrich) monomers were passed through an inhibitor removal column and stored over molecular sieves, and the styrene (Aldrich) monomer was fractionally distilled under vacuum prior to use. The matrix resin comprised a DGEBA-type epoxy and a diamine hardener. These were generously supplied by the manufacturers. The trade names and chemical structures are provided in Table 7-2.

Table 7-2. Chemical Products for the Synthesis of Epoxy Matrix.

Material	Chemical Formula	Trade Name
Epoxy prepolymer DGEBA (Dow Chemical)	$\text{H}_2\text{C}^{\text{O}}-\text{CH}-\text{CH}_2-(\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2$ $\text{Mn} = 348 \text{ g/mole } (n = 0.01)$	Tactix 123
Liquid diamine (Huntsman Chemical)	$\text{H}_2\text{N}-(\text{CH}_2)_3\text{O}-(\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CHO}}})_n-(\text{CH}_2)_3-\text{NH}_2$ $\text{Mn} = 306 (n = 3)$	Jeffamine D230

Interphase Design Using the Shear Lag Model with Interphase

Prior to synthesizing the copolymers for designed interphases, the shear lag model was used to select three interphase moduli that would be targeted for study. The objective was to choose three values representing a low (rubbery), intermediate (tough) and high (brittle) modulus interphase so that the effect of the interphase mechanics could be better elucidated. Figure 7-2 is a plot of the maximum shear stress versus the interphase thickness computed from the shear lag model for three different interphase moduli. These values represent the actual moduli of the interphases used. The intermediate modulus value, in particular, was arrived at after an iterative process to attain both the desired modulus and yield strength. The shear lag model parameters were chosen to replicate the conditions and material properties of the fiber and matrix and fiber-reinforced composites.

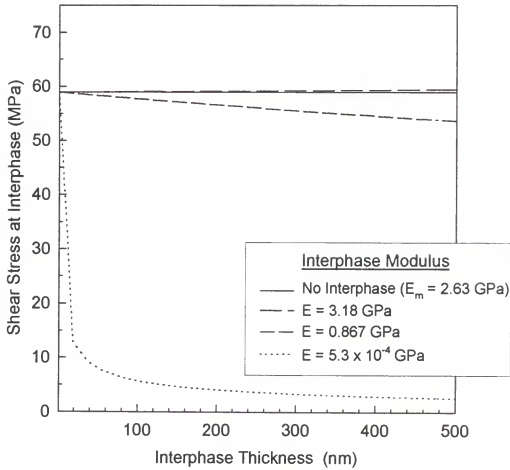


Figure 7-2. The effect of interphase thickness on the shear stress at the fiber/interphase margin computed from the shear lag model for three different interphase moduli.

For example, the fiber and matrix variables were selected to best represent the values of the aliphatic-amine cured epoxy and a UHMPE fiber (Spectra® 900). Thus, the shear modulus of the matrix, $G_m = 0.876$ GPa, is approximated as one third the tensile modulus assuming the Poisson's ratio is ca. 0.33, which is reasonable for most glassy polymers. Likewise, the fiber tensile modulus is equal to 80.9 GPa, as determined in chapter 6; the volume fraction is 0.6 as will be shown, and the fiber radius equal to $19\text{ }\mu\text{m}$ (Spectra® 900 fibers). The radius of the matrix is determined from the volume fraction of fibers according to

$$r_m = \left(\frac{r_f}{v_f} \right)^{1/2}$$

Figure 7-2 shows that the interphase modulus, E_i , influences the magnitude of the shear stress at the fiber/interphase margin, and hence, affects the stress transfer capability of the fiber/interphase/matrix system. As E_i decreases, the shear stress decreases more rapidly with increasing interphase thickness. The shear stress of the low (rubbery) modulus interphase, in particular, drops precipitously with thickness. This result is consistent with the preponderance of studies that show rubbery interphases reduce the reinforcement efficiency of both particulate and fiber-reinforced composites.^{50, 129, 130} When E_i equals 3.18 GPa, a value greater than E_m , the shear stress increases slightly with increasing interphase thickness, although the shear stress decreases with thickness when E_i equals 0.867 GPa. However, the difference in shear stress and corresponding stress transfer for these two cases is negligible ($< 5\%$) up to an interphase thickness of 200 nm. This suggests that the modulus of the interphase may be reduced to some extent without the loss of stress transfer. The remarkable result is that the intermediate modulus

interphase, exhibiting a modulus less than 1 GPa, attains 99% of the stress transfer efficiency of the high modulus interphase at an interphase thickness (10-20 nm) corresponding closely with that measured for hydroperoxide-initiated SAN grafts (Chapter 6).

Based on the properties of poly(styrene-co-cyclohexyl methacrylate-co-butyl acrylate) terpolymers discussed in Chapter 3, the addition of butyl acrylate to the brittle styrene/cyclohexyl methacrylate copolymer produces a similar modulus reduction as described above for $E_i = 0.867$ GPa. Moreover, the elongation to failure of the terpolymer increases by 1000% and the failure mechanism changes to a shear yielding type of deformation (Chapter 3). Thus, the interphase can be engineered to promote stress transfer and provide a mechanism of energy dissipation by varying the composition of the graft polymer.

Styrene/Acrylonitrile/Butyl Acrylate Copolymer Synthesis

The requirements of the copolymer graft were three-fold. First and foremost, a copolymer was sought that could be tailored to provide a range of mechanical properties, i.e. modulus and strength. Thus, a copolymer employing at least one high Tg monomer and another low-Tg monomer was necessitated. Second, since ESCA analysis was one of the few methods for detecting the very thin layer of polymer grafts, a monomer containing nitrogen as a marker was warranted. Hence, the use of acrylonitrile(AN) fulfilled this requirement as well as the need for a high Tg monomer. Finally, the copolymer needed to be soluble in toluene and tetrahydrofuran, the two solvents integral to the hydroperoxidation grafting process. This last aspect necessitated the partial substitution of acrylonitrile with styrene (S), another high Tg monomer. Thus, a terpolymer

comprising styrene, acrylonitrile and butyl acrylate monomers (S/AN/BA) was used to engineer interphases in UHMPE-fiber-reinforced epoxy composites.

Since the copolymer mechanical properties were characterized in bulk, rather than analyzing the grafts directly, it is imperative to recognize the differences in the reactivity ratios of the three monomers and hence, the corresponding composition drift during polymerization. Upon closer inspection of the hydroperoxidation grafting process described in Chapter 6, it is apparent that very low polymer conversions prevail. Thus, the theoretical conversions were first estimated based on the surface properties of UHMPE fibers, the maximum graft density and graft molar mass prior to performing bulk copolymerizations of S/AN/BA copolymers.

The minimum area consumed per grafted chain as approximated from Langmuir-Blodgett measurements of the maximum packing of closely packed alkane chains, is $0.2 \times 10^{15} \text{ cm}^2/\text{molecule}$.¹³¹ And based on the smooth topography of the UHMPE fiber (Spectra® 900) surface, the approximate specific surface area of these fibers is $1085 \text{ cm}^2/\text{g}$. Thus, it is possible using these two values to determine the number of grafting sites per gram of fiber. If, for example, a chain with molar mass, $100,000 \text{ g/mole}$, were grafted at every site, the maximum ratio of moles of monomer per gram of fiber can be calculated. For instance, if styrene monomer were grafted, 0.09 g of styrene per gram of UHMPE fiber would be needed. In chapter 6, a monomer loading of 30 g per 0.6 g of fiber was prescribed. This represents a monomer/fiber ratio of 50, which is nearly three orders of magnitude larger than the theoretical minimum amount of monomer needed. Furthermore, if this kind of grafting efficiency were achieved, there would be less than 1% conversion of monomer to polymer.

In this chapter the monomer/fiber loading was adjusted because of the large volumes required to graft onto fabric samples. In order to treat eight plies simultaneously in a 2000 ml reaction flask, the monomer/fiber loading was reduced to a value of 9. If 100,000 g/mole grafts were tethered at an optimum packing density the conversion would reach 1% exactly. Therefore, the levels of conversion during the synthesis of the bulk copolymers were maintained at less than 5%. This level is more pragmatic since a minimum of 0.5 grams is needed for evaluation, and helps ensure that the bulk properties of the copolymers are representative of the grafted copolymer chains.

The terpolymerization behavior of the S/AN/BA system has been studied at different degrees of conversion by Schellenberg and Hamann.¹³² At low degrees of conversion (2 mole percent), the dependence of the terpolymer composition was calculated from the monomer feed compositions based on the reactivity ratios of each monomer. There is considerable composition drift away from the BA portion of the diagram towards the line adjoining the ST/AN and ST/BA azeotropic compositions. This tendency intensifies the further the feed composition is from the connecting line. At compositions close to this line, the drift predominates toward the ST/AN azeotropic composition.¹³² Thus, it was necessary to estimate and compensate for the composition drift through appropriate selection of the feed composition.

Subsequent terpolymerizations were carried out under conditions analogous to the hydroperoxidation grafting procedure. The polymerizations were typically run in a round bottom flask containing the monomers and toluene with a monomer concentration equal to 50 wt%. A low concentration of AIBN (0.1 wt%) was used to further replicate the conditions of hydroperoxidation grafting, i.e., low initiator concentration. Prior to adding

the AIBN, the monomers were purged by bubbling nitrogen gas through the liquid mixture. The monomers were polymerized under gentle stirring conditions in a round bottom flask under a nitrogen atmosphere at 70°C for times of 60-90 minutes to maintain conversions below 5 wt%. The polymer was subsequently precipitated in cold hexane, dried under vacuum overnight at a temperature above the T_g, and analyzed by DSC, elemental analysis and tensile tests.

Characterization of S/AN/BA copolymers

The characterization of the copolymers entailed gel permeation chromatography (GPC), DSC, ESCA, elemental analysis and mechanical evaluation using tensile tests. GPC was performed on a Waters unit using polystyrene calibration standards in THF solvent. The details of the DSC and ESCA analysis techniques are described in Chapter 6.

The tensile properties of the copolymers were measured using an Instron 1122 mechanical tester with an 890 Newton load cell. The copolymer samples were prepared by hot-pressing at 150°C under 44,000 Newton load in a rectangular die between TFE-coated Kapton[®] sheets and chrome-finish steel plates to a thickness of ca. 0.30 mm. Samples were cut from the resulting film using a Type MIII die according to ASTM D638M. Samples for ESCA analysis were also cut from the pressed film. The two copolymers with T_g's above room temperature were conditioned one day at standard conditions, whereas the other copolymer was refrigerated to retain its shape prior to testing. Samples were subsequently tested at a rate of 10 %/min using a gage length of 25 mm.

Elemental analysis results were provided by the Department of Chemistry at the University of Florida. These were used to measure the atomic concentrations of carbon,

hydrogen and nitrogen at a standard error of 0.16%, 0.05% and 0.01%, respectively.

Assuming that oxygen comprises the total of the remaining weight, the relative percentages of styrene, acrylonitrile and butyl acrylate monomers were estimated. H-NMR was used to confirm these results.

Grafting UHMPE Fabrics by Hydroperoxide Surface Modification

As mentioned above, the hydroperoxide grafting procedure was scaled up to account for the larger quantities of fiber needed to process each composite laminate. A total of eight plies was treated during a single hydroperoxidation experiment, 7 plies for the fabrication of the composite laminate and an extra for surface characterization. Because of the large volume consumed by this much fiber, a 2000 ml reaction flask was used to house the hydroperoxidation and grafting reactions. Following the washing of the fibers in refluxing acetone and benzene (see Chapter 6), the fibers were immersed in an AIBN/benzene solution (0.05 M) at elevated temperatures through which oxygen was vigorously bubbled. Based on the calculations described previously, the amount of AIBN necessary to hydroperoxidize a minimum of one site for every 0.2 nm^2 of fiber surface is 7.4×10^{-15} grams per gram of fiber (Spectra[®] 900). Although a ratio of 0.37 in Chapter 6 was used, the larger volumes of solution necessary for these treatments resulted in an increase in the weight of AIBN to fiber weight to a value of 3.3. Thus, the hydroperoxidation treatment was initiated in a starting solution volume of 400 ml at 70°C. An additional 200 ml of AIBN/benzene solution was added after the first hour followed by an addition of 250 ml at the end of the second hour. The hydroperoxidation treatment was terminated at the end of three hours. As noted in Chapter 6, the replenishment of

AIBN/benzene solution ensures that the free radical supply is maintained since the half life of AIBN radicals is approximately 2-4 hours at 70°C-75°C.¹²²

Following the hydroperoxidation treatment, the fabric swatches were removed from the reaction flask and kept immersed in the hot AIBN/benzene solution while the flask was cleaned. The flask was then refilled with 500 ml monomer/toluene solution with a monomer concentration of 50 wt%. The weights of toluene and each of the three monomers was determined by the desired feed composition as well as their densities so that a solution volume of 500 ml was attained. The grafting reaction was carried out at 70°C for 15-16 hours while bubbling nitrogen gas through the monomer solution. Subsequently, the fabrics were washed thoroughly by washing and stirring in THF until clean. The THF was flushed twice daily. A Hewlett-Packard UV/VIS spectrometer was used to detect residual monomer, S/AN/BA homopolymer, or toluene. Although the washing process typically lasted 4-5 days, the UV/VIS provides confidence (up to 50 ppm residual contaminants) that the fibers were completely free of adsorbed polymer or monomer.

Some typical UV/VIS transmission profiles are shown in Figure 7-3. After the third wash, residual contaminants are detected and a significant change in the UV-cutoff is observed. After the seventh wash the transmission spectrum virtually superimposes that for the pure THF and there is no discernible difference in the UV-cutoff.

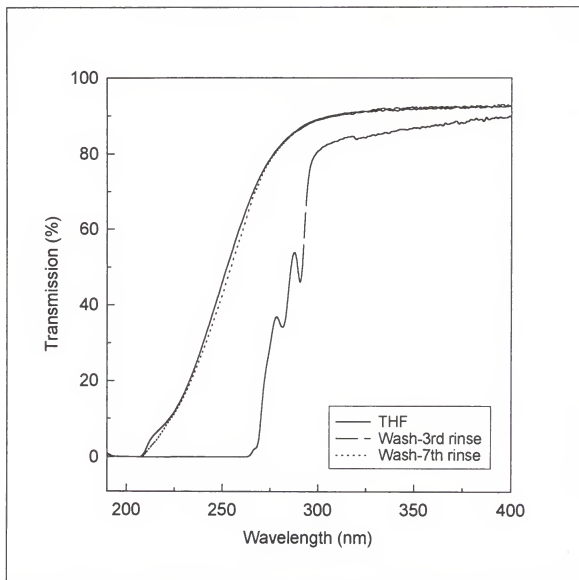


Figure 7-3. UV/VIS transmission spectra for wash solutions following S/AN/BA hydroperoxidation grafting.

Composite Fabrication

Woven, bidirectional fiber-reinforced composites (7-ply) were fabricated by a modified leaky mold technique. The technique, as described by Ladizesky and Ward, involved the use of an open-ended two-part mold.⁴⁷ In this work, the mold consisted of three parts: (i) the base plate, a 152.4 mm x 152.4 mm x 6.4 mm aluminum plate, (ii) the middle mold with cutout, a 152.4 mm x 152.4 mm x 19 mm block with 127 mm x 127 mm cutout and (iii) the top insertion piece. Figure 7-4 shows a schematic of the mold parts. The mold represents a modified leaky mold since the top part of the mold is not bolted to the other two pieces, although the base and middle plates were bolted together. Thus, it was designed to allow excess resin and air to vent out the top between the middle and top parts. The UHMPE fiber fabrics were also cut to 114 mm x 114 mm, a dimension smaller than the opening of the middle part. This allowed excess resin to thoroughly wet-out the fibers and ensured that trapped air was expunged from the fiber impregnated area. A computer spreadsheet was developed to calculate the amount of resin needed based on the weave thickness, areal density (weight of fiber per square inch), density of fibers, density of epoxy matrix, number of fiber layers (plies), and mold coverage of fibers (114 mm x 114 mm). The number of layers was chosen so that the resulting composite laminate thickness exceeded 2.5 mm, the thickness necessary to perform mechanical testing for the given flexure fixtures. Consequently, the amount of resin was calculated and multiplied by a factor of 2.8 to yield sufficient excess resin for low-void composites.

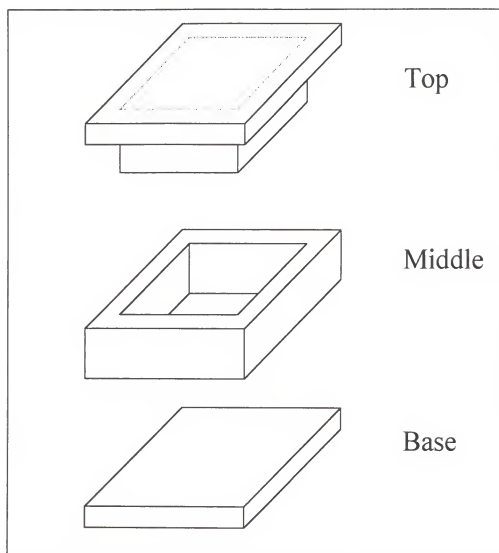


Figure 7-4. Schematic of the three part mold used to compression mold woven, bidirectional fiber-reinforced composites.

Before placing the fibers, each piece of the mold was cleaned thoroughly with citric acid cleaner (Stoner). Each part was then spray-coated with Stoner E455, a wax-based mold release.

The liquid matrix was prepared by weighing stoichiometric amounts of the Tactix 123 DGEBA-type epoxy and the Jeffamine D230 diamine hardener calculated using a computer spreadsheet based on the equivalent weights of each. For the seven-ply composites utilized here, the amount of resin totaled 70.72 grams (53.05 grams of epoxy and 17.67 grams of diamine hardener). The matrix components were then mixed in a 400 ml plastic beaker using an electric mixer and a steel, four-blade mixing blade at 400 RPM for 5 minutes. The liquid matrix was then degassed under vacuum for 1 hour. Prior to laying-up the composite, the bottom and middle parts of the mold were assembled with eight bolts. Using a 10 ml glass pipette, the resin was subsequently added in nine fractions. The fractions were calculated by taking the total amount of resin, subtracting five, and dividing the remainder by nine. The extra five grams was saved for last and added to the top of the laid-up composite. The composites were prepared by the wet lay-up technique in which the layers of fiber are laid down between layers of liquid epoxy in the bottom of the mold.

The lay-up of the composite was begun by releasing the first fraction of the liquid resin from the pipette dropwise onto the base plate of the mold. This was done carefully to avoid introducing air bubbles. The first fiber weave was then placed into the cutout of the mold over the newly formed puddle of liquid resin. Using a wooden roller, the wet-out of the fiber weave was assisted by advancing the roller slowly in the transverse and longitudinal directions, parallel to the fiber placement. The second fraction of liquid resin

was subsequently added to the top of the first weave, uniformly and dropwise over the area of the weave to promote rapid wet-out. The second weave was then meticulously placed into the mold over the first weave so that the fibers in the warp and weft of each layer were closely aligned. The wooden roller was again gently applied to the second weave to assist the impregnation of the fibers by the liquid matrix. This process was continued until seven layers were laid-up, and completed by adding the final fraction and the reserved excess of liquid resin to the top of the multi-layer composite.

Following the lay-up process, the bottom part of the mold, containing wetted-out fibers, was then degassed under vacuum for 15 minutes. A considerable amount of air was displaced during this step and the force exerted by the bubbles was sufficient to cause shifting of the fiber weaves relative to one another. This problem was allayed by pinning the corners of the composite using straight pins during the first degassing step. After degassing the first time, the straight pins were removed and the top part of the mold was gently placed into the bottom two-thirds of the mold without applying pressure. The complete mold was degassed an additional fifteen minutes. Finally, the whole mold was placed between hot platens and compression molding was commenced. The pressure was applied in a single cycle and during the initial stage of compression the excess resin was squeezed out of the mold. Because of the amount of excess resin, precautions were taken to contain the leakage of liquid epoxy.

The composites were compression molded at an initial force of 3500 Newtons. The epoxy was cured during the compression stage at 100°C for two hours. The thickness of most composites was maintained between 2.6 and 2.9 mm and the corresponding volume fraction of fibers was kept between 0.55 and 0.58.

The composite plaques were cut using a water jet cutter (Advanced Technology Manufacturing, Sanford, FL) with a water stream generated at a pressure of 50 kpsi through a 0.2 mm diameter orifice. The resulting 114 mm x 114 mm fabric-reinforced composite sample was cut into samples for flexural testing (5 specimens), impact testing (5 specimens), short beam shear test (6 specimens), DSC (5 specimens) and density measurements (3 specimens). Since there was some non-uniformity in the plaque thickness after compression molding, careful attention was given to the placement of the plaque during water jet cutting. The orientation of different plaques during subsequent cutting operations was matched to the original orientation.

The thermal response curves of the UHMPE-fiber reinforced composites were obtained using a Seiko model DSC 220C (heat-flux type). The samples (3 mm x 2.8 mm x 1.5 mm) were analyzed at a heating rate of 10 °C/min under a dry nitrogen atmosphere maintained at a flow rate of approximately 100 ml/min. Samples were enclosed in crimped aluminum pans before analysis. The enthalpy of melting was quantified using the thermal analysis software.

The density of the composite materials were measured by water displacement according to ASTM 792. Ultra-pure water was used to measure the density of square samples (20 mm x 20 mm x 2.8 mm).

The flexural modulus of the woven, bidirectional fiber-reinforced composites was measured on an Instron mechanical tester with a 5000 kg reversible load cell. Rectangular composite beams (65 mm x 12.3 mm x 2.8 mm) were tested under a three-point bend configuration according to ASTM D790 at a crosshead rate of 1 mm/min with a support span of 50 mm. This ensured a span-to-depth ratio greater than 16. Since the maximum

permissible strain is 0.05, the tests were ceased at a center-beam deflection of 6-7 mm. The diameter of the support and loading rods was 6 mm and 4 mm, respectively.

The interlaminar shear strength was measured using the short beam shear test according to ASTM D2344. The rectangular short beams (22 mm x 12.5 mm x 2.7 mm) were tested at a crosshead rate of 1 mm/min with a support span of 10 mm. This ensured a span-to-depth ratio of less than 4. The diameter of the support and loading rods was 4 mm.

The impact strength of composite beams was measured on a Tinius-Olson pendulum-type impact tester capable of delivering a maximum energy of 5.65 J. The impact tester conforms to the specifications given in ASTM D256 in terms of the clamping base dimensions, height of impact point, vertical falling distance and center of percussion. Prior to testing the composite beams, the energy lost due to friction and inertia of the energy indicating mechanism were determined per the procedure given in ASTM D256. These values were used to calculate the machine correction and create a table of the impact strength versus the energy-indicator value. The impact strength of unnotched specimens was subsequently measured by securing a composite specimen (65 mm x 12.3 mm x 3.0 mm) in the clamping device and releasing the pendulum arm. Unnotched samples were used, as prescribed by Ward and Ladizesky, because of the notch-insensitivity of UHMPE fiber composites and the very high strengths that prevent failure in conventional notched impact tests.¹³³ Consequently, the samples failed by a hinge-type mode of failure and the impact strengths represent the energy absorbed upon the first impact to produce this result.

Results and Discussion

S/AN/BA Copolymers

Three interphase polymers were sought in order to study the effect of the interphase mechanics on the composite performance. These included (i) a high-T_g, high modulus ($E \approx 3$ GPa) interphase, (ii) a mid-T_g, intermediate modulus ($E \approx 1$ GPa) interphase with a correspondingly lower shear strength and (iii) and a very low-T_g, low-modulus and rubbery interphase. Since the butyl acrylate (BA) monomer represented the low-T_g monomer, its relative fraction was increased or decreased to lower or raise the T_g, respectively. In addition, a concentration of acrylonitrile sufficient for detecting nitrogen by ESCA analysis was targeted in each copolymer composition. The phase drift inherent to this terpolymer system necessitated several iterations to establish the desired composition and mechanical properties for the Mid-T_g interphase terpolymer. In particular, a modulus sufficient for stress transfer as predicted from the shear lag model was sought. In addition, a yield strength value lower than the ILSS of the High-T_g interphase material was targeted. It was postulated that the Mid-T_g interphase, properly designed, would display shear yielding prior to interfacial debonding. The feed compositions, T_g, stress at yield and modulus of the supplemental Mid-T_g terpolymers are listed in Table 7-3. The final Mid-T_g composition and properties are discussed below.

Figure 7-5 shows the feed and final compositions, connected by an arrow, for each of the three interphase copolymers. The polymer composition drifts toward the line adjoining the S/AN and S/BA azeotropic compositions. The interphase terpolymers are

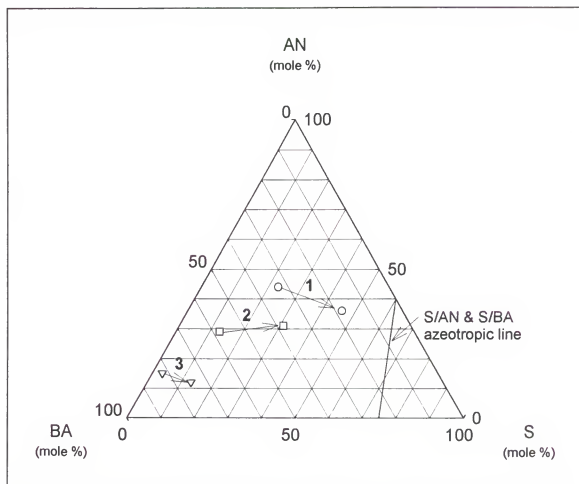


Figure 7-5. The composition drift associated with terpolymerizations of S/AN/BA copolymers (conversions less than 5%). The numbers 1, 2 and 3 denote the High Tg ($T_g = 78^\circ\text{C}$), Mid Tg ($T_g = 38^\circ\text{C}$) and Low Tg ($T_g = -14^\circ\text{C}$) S/AN/BA terpolymers, respectively.

referred to here as High Tg ($T_g = 78^\circ\text{C}$), Mid Tg ($T_g = 38^\circ\text{C}$) and Low Tg ($T_g = -14^\circ\text{C}$) and will be referred to herein by this nomenclature. Table 7-4 lists the atomic concentrations determined from elemental analysis as well as the calculated fractions of each monomer and the T_g of each of the terpolymers. H-NMR was used to validate the elemental analysis, in particular the ratio of styrene to butyl acrylate monomers. For example, the calculated mole ratio of styrene to butyl acrylate determined from elemental analysis for the High-Tg terpolymer was 2.6, exactly the ratio determined from H-NMR analysis.

Table 7-3. The S/AN/BA terpolymer compositions and corresponding thermal and mechanical properties evaluated during multiple iterations towards the final Mid-Tg composition.

S/AN/BA Terpolymer (Feed Composition, wt%)	T_g	Modulus (GPa)	Stress at Yield (MPa)
9/11/80	20°C	—	—
10/12/78	24°C	—	—
11/13/76	28°C	0.18	4
12/14/74	33°C	0.36	6
13/15/73	36°C	0.58	7
14/16/71	40°C	1.9	31

The feed and measured compositions along with the tensile properties of each of the S/AN/BA terpolymers are listed in Table 7-5. The composition drift is numerically illustrated by the change in feed and measured compositions for each monomer. In addition, the relevant tensile properties are compiled and show the general trend of decreasing modulus and yield strength with increasing BA content. At the composition corresponding with the High-Tg terpolymer, the modulus is characteristic of a glassy

Table 7-4. Results from Elemental Analysis of S/AN/BA Terpolymers (provided by the Department of Chemistry, University of Florida).

Polymer Feed Composition (mole%)	Elemental Analysis of Polymer <5% Conversion (wt%)				Calculated Composition			Measured Tg
	N	C	H	O	S wt% (mole%)	AN wt% (mole%)	BA wt% (mole%)	
High Tg (23/44/33)	5.7	80.07	7.93	6.3	53 (46)	21 (36)	26 (18)	78°C
Mid Tg (13/29/58)	4.4	75.33	8.29	11.94	41 (31)	17 (31)	42 (38)	38°C
Low Tg (3/15/82)	1.55	69.24	9.04	20.17	12 (13)	5 (12)	83 (75)	-14°C

polymer below its Tg and the tensile response, as shown in Figure 7-6, exhibits a brittle-type failure. For the mid-Tg terpolymer, the BA content is sufficient to reduce the modulus to just below 1 GPa. More importantly the yield strength decreases to a value of 15.7 MPa. In terms of engineering a synergistic interphase that provides both stress transfer and a mechanism of energy dissipation, this terpolymer represents a promising candidate. As shown by the shear lag analysis, an interphase modulus of 0.867 GPa is mechanically adequate to allow sufficient stress transfer, only sacrificing 5% of the transfer capability up to an interphase thickness of 200 nm. And as Figure 7-6 shows, the ductile behavior of this polymer would promote interphase yielding when the stress exceeds the shear or yield stress, depending on the prevailing stress conditions, of this terpolymer. As the BA content is increased further, the terpolymer modulus and yield strength drop precipitously. Consequently, this terpolymer borders between a viscous fluid and a rubbery solid. Despite the ambiguity, this terpolymer will be used to demonstrate the

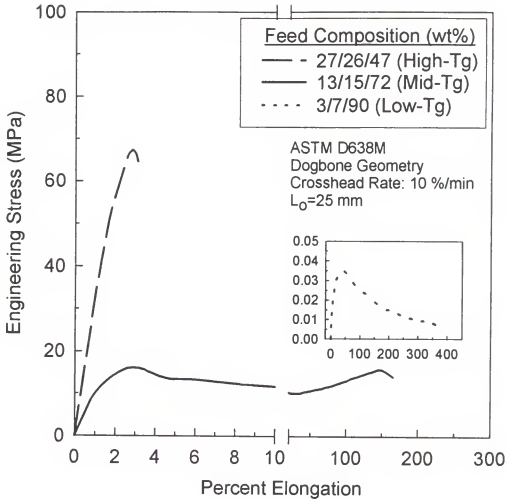


Figure 7-6. Tensile stress-elongation response of High-Tg, Mid-Tg and Low-Tg S/AN/BA terpolymers. Note that a break in the percent elongation axis is provided to show the elongation to failure of the Mid-Tg terpolymer. An insert is also included to illustrate the tensile response of the Low-Tg interphase terpolymer.

effect of decreasing interphase modulus and yield strength on the composite ILSS, flexural modulus and impact strength.

Table 7-5. The Feed and Final Compositions Determined by Elemental Analysis along with the Relevant Mechanical Properties of S/AN/BA Terpolymers.

S/AN/BA Terpolymer	Composition (mole%)			Modulus (GPa)	Yield Strength (MPa)
	Styrene	AN	BA		
High Tg (78°C)					
Feed	23	44	33		
Measured	46	36	18	3.18	81.7
Mid Tg (38°C)					
Feed	13	29	58		
Measured	31	31	38	0.867	15.7
Low Tg (-14°C)					
Feed	3	15	82		
Measured	13	12	75	5×10^{-4}	4×10^{-2}

S/AN/BA Grafts

The hydroperoxidation grafting process is very surface-limited in nature because of the highly crystalline structure of the UHMPE fibers and their poor solubility with most organic solvents and monomers. Consequently, the linear, polymeric grafts comprise a layer that is inherently thin, the thickness of which is related to the molar mass of the grafts and the molecular dimensions of the grafted chain (see Chapter 6), and difficult to characterize by conventional means. Characterization of the grafting efficiency, for instance, is not conducive to gravimetric analysis. Based on the analysis given in Chapter 6, the weight gain corresponding with a graft layer that is 10-30 nm thick is a negligible 0.3 wt%. ESCA analysis, on the other hand, is a convenient method to probe the first 50-

100 angstroms of the surface, and hence detect and quantify the grafts. By comparing the surface compositions of the bulk S/AN/BA terpolymers and the S/AN/BA-grafted UHMPE fibers, the grafting efficiency can be assessed assuming the surface chemistry of the grafts juxtaposes that of free polymer chains.

The bulk and surface atomic concentrations of the three S/AN/BA terpolymers are listed in Table 7-6. The bulk atomic concentration of nitrogen decreases and the oxygen increases through the series, High-Tg, Mid-Tg and Low-Tg terpolymers, respectively. This is associated with the decreasing AN content and the increasing BA contents through the series. The surface atomic concentrations are also listed in Table 7-6. The surface nitrogen content also decreases, whereas the oxygen content increases through the series High-Tg, Mid-Tg and Low-Tg. However, the nitrogen concentration is lower than in the bulk. With the exception of the Low-Tg terpolymer, the oxygen concentration is higher at the surface than in the bulk. This result is somewhat expected since it would be energetically favorable, based on the cohesive energy densities of BA and AN, for the butyl acrylate segments to preferentially organize at the surface over acrylonitrile.⁸⁵ All three samples exhibited small amounts (< 1%) of silicon.

The grafting efficiency can subsequently be computed by comparing the surface nitrogen concentration of S/AN/BA-grafted fibers, as measured by ESCA analysis, with that of the terpolymers. Table 7-7 lists the surface atomic concentrations of both the terpolymers and the treated UHMPE fibers. An interesting feature of the ESCA high resolution C(1s) spectra of the S/AN/BA-grafted fibers was the appearance of a shoulder along the main peak. As was shown in Chapter 3 for poly(butyl acrylate)-grafted UHMPE fibers, the shift corresponds with the presence of ester side groups in butyl acrylate-

containing grafts. The oxygen induces a C(1s) peak shift to higher binding energies by ca. 1.5 eV per shared electron pair between carbon and oxygen.⁸² This shoulder was evident in each of the S/AN/BA-grafted fiber spectra, but was not as discernible in either the washed nor the hydroperoxidized-only (HPX-only) fiber spectra. Note that the term "Washed" is used to designate as-received fibers that were washed in refluxing acetone and then benzene.

Table 7-6. Bulk and Surface Atomic Concentrations of the S/AN/BA Terpolymers Determined by Elemental and ESCA Analysis.

S/AN/BA Terpolymer	Elemental Analysis of Bulk <5 % Conversion (atomic concentration, %)			ESCA Analysis of Surface < 1 % Conversion (atomic concentration, %)		
	C	N	O	C	N	O
High Tg	89.4	5.3	5.3	88.3	3.5	8.2
Mid Tg	86.8	4.4	8.8	83.7	1.4	13.4
Low Tg	80.4	1.4	18.2	81.7	1.2	17.1

Table 7-7. ESCA Surface Analysis of S/AN/BA-grafted UHMPE Fibers and Terpolymers for the Determination of the Grafting Efficiency.

UHMPE Fiber	UHMPE Fibers Atomic Concentration (%)			S/AN/BA Copolymer Atomic Concentration (%)			Grafting Efficiency $\frac{N_{\text{graft}}}{N_{\text{copolymer}}}$
	C	N	O	C	N	O	
Washed	90.0	—	10.0	—	—	—	—
HPX-only	93.6	—	6.0	—	—	—	—
S/AN/BA grafted:							
Low-Tg	91.2	0.28 ± 0.19	8.3	81.7	1.2	17.1	0.23
Mid-Tg	95.6	0.35 ± 0.02	4.0	83.7	1.4	13.4	0.25
High-Tg	93.7	1.2 ± 0.1	5.2	88.3	3.5	8.2	0.34

The grafting efficiency is represented by the ratio of the surface nitrogen contents of the grafts and the terpolymer. Hence, a ratio equal to one denotes a grafted surface that is identical, chemically and conformationally, to the bulk terpolymer surface. The grafting efficiency of the High-Tg, Mid-Tg and Low-Tg S/AN/BA grafts varies between 0.23 and 0.34. These values represent the averages of three measurements and are much lower than the grafting efficiency of SAN-grafted UHMPE fibers, equal to 0.92 (see Chapter 6). The only difference in the hydroperoxidation and grafting procedures, with the exception of the grafted polymers, is the monomer-to-fiber ratio. In the SAN-grafting experiments, the monomer-to-fiber ratio was maintained at 50 whereas the ratio was reduced to 9 in these experiments, albeit for practical reasons. If a ratio of 50 were used, the volume of monomer and toluene necessary to treat eight plies would exceed 2 liters. Despite the reduction in graft fraction, it will be shown in the following sections that the grafts strongly influence the reinforcement and impact characteristics of the composites.

An additional experiment was performed to evaluate the effect of hydroperoxidation temperature on the grafting efficiency of the Mid-Tg grafts. A set of fabric swatches was hydroperoxidized at 50°C instead of the usual hydroperoxidation temperature of 70°C, with all other conditions kept the same. Following the hydroperoxidation step, the fibers were grafted with the Mid-Tg terpolymer according to the prescribed conditions. Thus, two sets of Mid-Tg S/AN/BA-grafted UHMPE fibers were obtained, one with a high graft efficiency ($T_{HPX} = 70^{\circ}\text{C}$) and the other with a low grafting efficiency ($T_{HPX} = 50^{\circ}\text{C}$). The extent of hydroperoxidation was visually apparent following the completion of the three-hour treatment in the AIBN/benzene solution. When the fibers were hydroperoxidized at 70°C, the AIBN/benzene solution darkened

steadily over time and displayed a dark yellow color by the completion of the treatment. In contrast, the solution appeared a much lighter shade of yellow following the hydroperoxidation at 50°C. The color was presumably associated with the formation of free radical-related complexes, probably with benzene. For example, Mattson *et al.* showed that xylene was a less effective solvent for solution grafting than chlorobenzene because it forms a stable radical complex in solution.⁷⁵

The effect of hydroperoxidation temperature on the grafting efficiency is quantified in Table 7-8. These values again represent the averages of three separate measurements. Although the nitrogen concentrations are low, the magnitudes of the peaks corresponding with an ejected N1s orbital electron (399 eV) typically exceeded 1600 counts in comparison to the peak-to-peak noise level of ca. 400-600 counts. These results indicate that the grafting efficiency is increased over 50% when the hydroperoxidation temperature is raised 20°C. As mentioned previously, the half life of AIBN is 2-4 hours at 70°C-75°C.¹²¹ Since the decay of AIBN can be expressed by an Arrhenius-type relationship, the general rule-of-thumb is that the rate is halved for every decade increment in temperature. Thus, a much larger drop in the grafting efficiency would be anticipated. This disparity is probably related to the fact that there exist multiple orders of magnitude excess of AIBN during the hydroperoxidation treatment. Also, the formation of stable free radical complexes with the benzene solvent may be less favorable at lower temperatures. Thus, a greater fraction of the AIBN radicals would be available for interactions with the fiber surface at lower temperatures. Another unexpected result was related to the oxygen concentration of the Mid-Tg ($T_{HPX}=50^{\circ}\text{C}$)-grafted fiber. When the hydroperoxidation temperature was decreased, the oxygen content increases. Since

there was no silicon observed above the detection limits, this result implies that the surface oxidation increases but the grafting efficiency decreases when the temperature is lowered. The ramifications of these results on the mechanical and interfacial properties appears to be graft-dominated and will be described in more detail below.

Table 7-8. Effect of Hydroperoxidation Temperature on the Grafting Efficiency.

<i>UHMPE Fiber</i>	UHMPE Fibers Atomic Concentration (%)			S/AN/BA Copolymer Atomic Concentration (%)			Grafting Efficiency
	C	N	O	C	N	O	$\frac{N_{\text{graft}}}{N_{\text{copolymer}}}$
Washed	90.0	—	10.0	—	—	—	—
HPX-only	93.6	—	6.0	—	—	—	—
S/AN/BA grafts:							
Mid-Tg ($T_{\text{HPX}}=50^{\circ}\text{C}$)	92.5	0.22 ± 0.11	7.2	83.7	1.4	13.4	0.16
Mid-Tg ($T_{\text{HPX}}=70^{\circ}\text{C}$)	95.6	0.35 ± 0.02	4.0	83.7	1.4	13.4	0.25

S/AN/BA-grafted UHMPE Fiber-Reinforced Composites

The weight fraction (w_f) of fibers was determined utilizing DSC to measure the enthalpies of melting of both the UHMPE fibers (Spectra® 900) and the composite samples. The w_f was determined according to

$$w_f = \frac{\Delta H_c}{\Delta H_f}$$

where ΔH_f represents the enthalpy of melting of UHMPE fibers analyzed separately, and ΔH_c the enthalpy of melting of fibers present in a composite sample. Hence, this method was beneficial for determining the exact weight fraction (w_f) of fibers since voids do not contribute to the DSC signal. Figure 7-7 shows typical thermal response curves for both a

composite and a fiber sample. In the top portion of the image, the DSC signal is plotted versus temperature. The peak exhibited by each curve is associated with the melting of polyethylene crystallites in the UHMPE fiber. The integrated area of the peak corresponds with the enthalpy of melting. In the bottom half of the figure, a DDSC response curve is plotted versus temperature for the composite sample, which represents the first derivative of the DSC-temperature spectrum. This plot was used to determine the onset of melting and the temperature at which the crystallites are fully melted. Hence, the dashed line across the DSC-temperature spectrum of the composite confines the area of the peak associated with fiber melting.

The fiber volume fraction, v_f , and composite theoretical density, ρ_c , were subsequently calculated according to

$$v_f = \frac{w_f / \rho_f}{(w_f / \rho_f) + (1 - w_f) / \rho_m}$$

$$\rho_c = \rho_f v_f + \rho_m (1 - v_f)$$

where the densities of the Spectra[®] 900 fiber and the D230/Tactix 123 epoxy matrix, ρ_f and ρ_m , are 0.97 g/cm³ and 1.1567 g/cm³, respectively. In addition, if the measured density and the theoretical density are compared, the volume fraction of voids can be estimated according to

$$v_v = \frac{\rho_c - \rho}{\rho_c}$$

in which ρ denotes the measured density. The v_f , theoretical density, measured density and calculated volume fraction of voids for each of the fiber-reinforced composites are

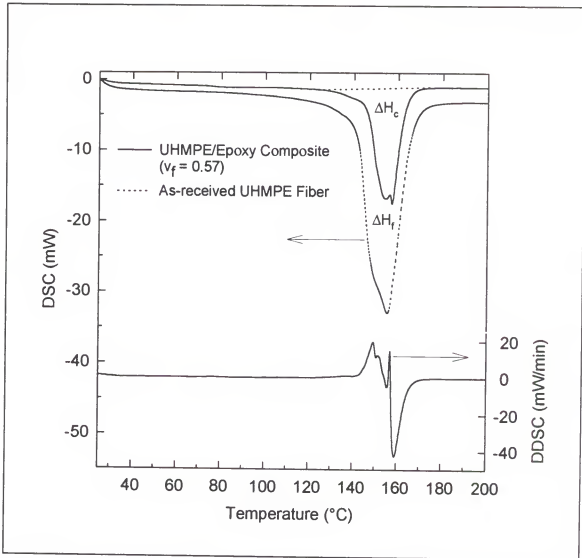


Figure 7-7. Thermal response curves for as-received UHMPE fibers and a UHMPE fiber-reinforced epoxy composite sample. The top portion of the figure shows the DSC signal-temperature spectra. The peak is associated with the melting of polyethylene crystallites in the fibers. In the bottom half of the figure, the DDSC-temperature response is shown, which represents the first derivative of the DSC-temperature curve. The DDSC was used to determine the melting onset and completion temperatures. The w_f of fibers was determined using the ratio of ΔH_c and ΔH_f .

listed in Table 7-9. The v_f and ρ_c values represent the averages, typically, of five measurements, whereas the densities and v_v values represent the averages of two to three measurements. The range of v_f 's from DSC measurements provides relatively good agreement with those calculated (0.57-0.60) for a composite, 2.8-3.0 mm thick. These measurements also indicate that the composites contain comparable fiber loadings, and that the void contents are not excessive, and maintained below 2% by the compression molding technique.

Table 7-9. DSC and Density Measurements of UHMPE-fiber Reinforced Epoxy Composites for the Determination of v_f and v_v .

<i>Fiber Reinforcement</i>	<u>DSC Measurements</u>		<u>Density Measurements</u>	
	v_f	ρ_c	ρ	v_v
Washed	0.57 ± 0.02	1.0503	1.0334 ± 0.005	0.0161
HPX-only	0.57 ± 0.02	1.0484	1.0326 ± 0.007	0.0151
S/AN/BA grafted:				
Low-Tg	0.54 ± 0.02	1.0559	1.0373 ± 0.002	0.0176
Mid-Tg	0.56 ± 0.00	1.0521	1.0367 ± 0.002	0.0146
($T_{HPX}=50^\circ\text{C}$)				
Mid-Tg	0.56 ± 0.00	1.0518	1.0357 ± 0.008	0.0153
($T_{HPX}=70^\circ\text{C}$)				
High-Tg	0.58 ± 0.01	1.0492	1.0413 ± 0.008	0.0075

The flexural response of the woven, bidirectional UHMPE fiber-reinforced epoxy composites is shown in Figure 7-8. The composites do not fail within the permissible range of deflection (ASTM D790) for a three point bending mode. Consequently, the stress-deflection curves are only displayed up to a deflection of 3.7 percent, at which the tests were ceased. The curves exhibit a linear response up to the proportional limit,

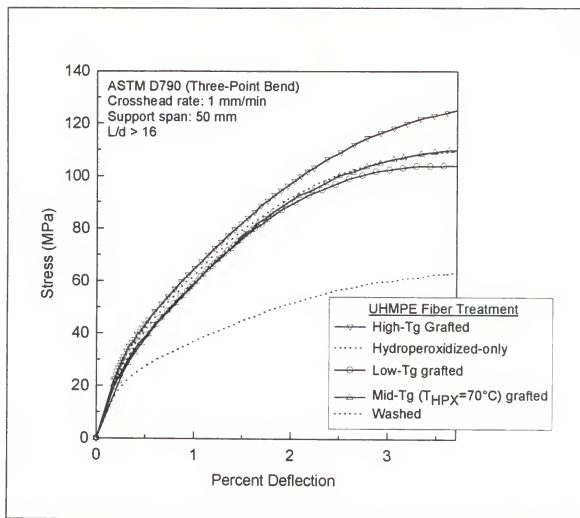


Figure 7-8. Flexural response of UHMPE fiber/epoxy composites (plain woven fibers, 7plies).

beyond which they are nonlinear with a different slope depending on the fiber surface condition.

The modulus, stress and deflection at the proportional limit as well as the stress at 5 mm deflection are listed in Table 7-10. The incorporation of washed UHMPE fibers increases the flexural modulus from that of the epoxy resin, $E_m = 3.24$ GPa, to a value of 8.85 GPa. The addition of S/AN/BA-grafted UHMPE fibers increases the modulus further. The High-Tg S/AN/BA interphase results in a 37%, statistically significant increase ($\alpha = 0.05$) in the modulus compared with the Washed-fiber composite. This was expected after visual inspection of the composites. Whereas the High-Tg composite appeared translucent, indicative of good fiber wet-out, the Washed-fiber composite was bright white in appearance. Similarly, the HPX-only and the other S/AN/BA-grafted fiber-reinforced composites were also translucent in appearance. The modulus decreased by 12%, compared with the High-Tg interphase, when HPX-only and Low-Tg interphase surface treatments were used. As discussed in Chapter 6, the HPX-only surface is highly oxidized and comprises surface functional groups such as hydroxyls, carbonyls, carboxylic acids, etc. These improve fiber wet-out and possibly provide sites for chemical bonding with the matrix. However, the results from the High-Tg composite indicate that the grafted surface, containing a lower concentration of chemically reactive groups, provides better reinforcement. Surprisingly, the Low-Tg interphase provides significantly better ($\alpha = 0.05$) reinforcement, in terms of the modulus, than the Mid-Tg interphase. However, the strength characteristics of the Mid-Tg interphase, i.e., the proportional stress and the stress at 5 mm deflection, are not significantly different from those for the Low-Tg interphase. The proportional stress of the other composites falls in line with the modulus

values. In particular, the High-Tg interphase provides a 60% improvement in the proportional stress compared with the Washed-fiber composite. The Low-Tg and Mid-Tg interphases provide over a 40% enhancement in the proportional stress, while the HPX-only composite exhibits a 28% improvement. The variation in the proportional deflection is not statistically significant between composites, with the exception of the High-Tg interphase, which shows a 30% increase compared with the Washed-fiber composite. Lastly, the stress at 5 mm deflection for the Low-Tg, Mid-Tg and HPX-only composites are equivalent, each showing ca. 66% increase compared with the Washed-fiber composite. The High-Tg composite shows a remarkable 95% rise in the stress at 5 mm deflection against the Washed-fiber composite.

Table 7-10. Flexural properties of UHMPE fiber-reinforced epoxy composites ($E_m = 3.24$ GPa).

<i>UHMPE Fiber Treatment</i>	Modulus (GPa)	Proportional Limit		Stress @ 5 mm Deflection (MPa)
		Stress (MPa)	Deflection (%)	
Washed	8.85 ± 0.84	14.0 ± 1.4	1.6 ± 0.3	61.5 ± 1.7
Low-Tg	10.7 ± 0.8	20.1 ± 2.3	1.9 ± 0.2	102 ± 2
Mid-Tg	9.58 ± 0.24	19.7 ± 3.7	1.8 ± 0.4	105 ± 3
HPX-only	10.6 ± 0.6	17.9 ± 2.9	1.7 ± 0.4	104 ± 12
High-Tg	12.1 ± 0.7	22.4 ± 1.6	2.1 ± 0.2	120 ± 3

The effect of grafting efficiency on the mechanical properties of the UHMPE fiber-reinforced composites was evaluated using the Mid-Tg interphase composites. As described above, the Mid-Tg S/AN/BA-grafted fibers were hydroperoxidized at two different temperatures (50°C and 70°C) to vary the grafting efficiency. Those fibers hydroperoxidized at 70°C exhibited a grafting efficiency over 50% greater than the fibers

hydroperoxidized at 50°C. The effect of grafting efficiency on the flexural response is substantial (Figure 7-9). The mechanical properties are compared in Table 7-11. Specifically, the Mid-Tg ($T_{HPX}=50^{\circ}\text{C}$) composite shows a marked decrease in the modulus compared to the Mid-Tg ($T_{HPX}=70^{\circ}\text{C}$) composite. This result is statistically significant ($\alpha = 0.05$), and the value is surprisingly close to the modulus of the Washed-fiber composites. Hence, the lower grafting efficiency causes a reduction in the stress transfer characteristics in terms of the modulus. There is also a concomitant drop-off in the proportional stress and the stress at 5 mm deflection of the Mid-Tg ($T_{HPX}=50^{\circ}\text{C}$) composite. The values each decrease ca. 30% compared with the Mid-Tg ($T_{HPX}=70^{\circ}\text{C}$) composite. However, the resulting values are not compromised to the level of the Washed-fiber composites. This outcome suggests that the factors governing the stress transfer and strength-related properties are different. It also supports the idea that the interfacial properties can be tailored through control of the graft attachment density.

Table 7-11. Effect of Grafting Efficiency of Mid-Tg S/AN/BA-grafted UHMPE Fibers on the Flexural Properties of Fiber-reinforced Composites.

<i>UHMPE Fiber Treatment</i>	Modulus (GPa)	Proportional Limit		Stress @ 5 mm Deflection (MPa)
		Stress (MPa)	Deflection (%)	
Washed	8.85 ± 0.84	14.0 ± 1.4	1.6 ± 0.3	61.5 ± 1.7
Mid-Tg ($T_{HPX}=50^{\circ}\text{C}$)	8.81 ± 0.32	15.4 ± 1.7	1.5 ± 0.1	71.5 ± 1.4
Mid-Tg ($T_{HPX}=70^{\circ}\text{C}$)	9.58 ± 0.24	19.7 ± 3.7	1.8 ± 0.4	105 ± 3
HPX-only	10.6 ± 0.6	17.9 ± 2.9	1.7 ± 0.4	104 ± 12

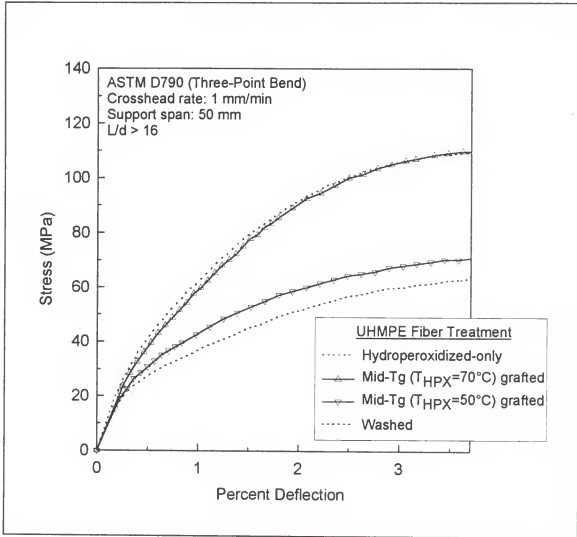


Figure 7-9. Effect of grafting efficiency of Mid-Tg S/AN/BA-grafted UHMPE fibers on the flexural response of fiber-reinforced composites (plain woven, 7 plies). The grafting efficiency is increased 50% when the hydroperoxidation temperature is raised 20°C .

Typical short beam shear-deflection curves are shown in Figure 7-10 for the UHMPE fiber-reinforced composites. With the exception of the Washed-fiber composite, the composites exhibit a linear response up to the interlaminar shear stress (ILSS), at which the stress plateaus as the fiber plies delaminate and fiber/matrix debonding commences. The ILSS was calculated according to the ASTM method by

$$\text{ILSS} = 1.5 \cdot \frac{(P/2)}{w \cdot d}$$

where P denotes the plateau load, w the composite width and d the depth. The Washed-fiber composite did not exhibit a plateau load, rather two non-horizontal regions were observed in the shear-response curve. Consequently, the interlaminar failure load was determined from the intersection of the tangents to the initial and final portions of the shear-response curve. The ILSS values of the UHMPE fiber-reinforced composites are listed in Table 7-12. Similar values have been reported by Kaplan *et al.* and Brown *et al.* for woven, bidirectional UHMPE (Spectra®)/epoxy composites.^{1, 17} The ILSS of the High-Tg interphase composite shows a remarkable improvement, exceeding 110%, over the Washed-fiber composites. As the interphase Tg modulus and yield strength decrease, so does the ILSS. Furthermore, the changes in the ILSS through the series, Low-Tg, Mid-Tg and High-Tg, are statistically significant ($\alpha = 0.05$) with each incremental increase. Not surprisingly, the trends in stress at 5 mm deflection correlate best with the ILSS values. The ILSS of HPX-only composites exhibit a similar improvement to the High-Tg composites. It seems that there is a maximum achievable ILSS. This result is surprising since the trends observed in the flexural properties strongly insinuate that the adhesion of the High-Tg interphase exceeds the HPX-only treatment. In fact, the

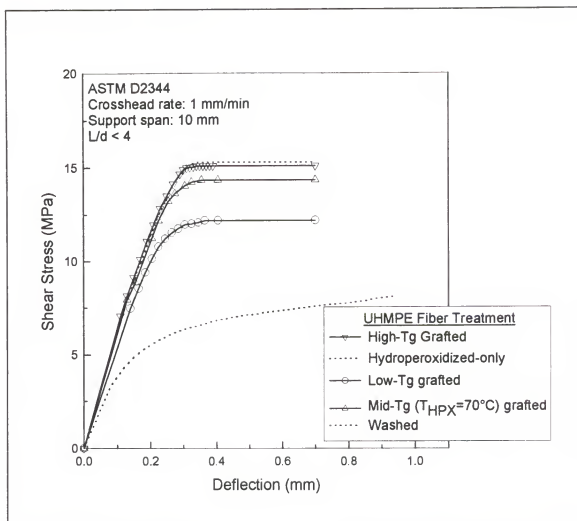


Figure 7-10. Typical short beam shear-response curves for UHMPE fiber-reinforced composites.

adhesion is better. Instead, this result seemingly indicates that the interfacial strength of these two composites is greater than that of the matrix. The matrix, in this case, would represent the weak link, and cohesive failure, rather than interfacial failure, would predominate under shear loading.

Table 7-12. ILSS of UHMPE Fiber-reinforced Composites.

UHMPE Fiber Treatment	ILSS (MPa)
Washed	6.89 ± 0.49
Low-Tg	12.2 ± 0.7
Mid-Tg	13.5 ± 0.7
HPX-only	14.6 ± 0.5
High-Tg	14.7 ± 0.7

A similar result was observed by Brown *et al.* for UHMPE fibers (Spectra® 900) surface modified by ammonia plasma treatments.¹⁷ In that case, the ILSS increased with treatment time from 5.7 MPa for untreated fibers up to a value of 11.1 MPa at 1 minute and 11.8 MPa at 2 minutes. After 10 minutes the ILSS leveled off although the degree of surface amination and the flexural modulus and strength continued to increase with treatment time.

Although the shear strengths of neither the interphase terpolymer nor the matrix were determined, it is possible to calculate the shear strength, τ_s , from the tensile yield strength, σ_y , using the von Mises criterion:

$$\tau_s = \frac{\sigma_y}{\sqrt{3}}$$

This approach has been used to compare the interfacial shear strength of fiber-reinforced composites with the matrix shear strength.⁶ However, large deviations between these two values has led to the empirical determination that the interfacial chemistry, stoichiometry and hence, the mechanical properties of the matrix can be quite different in the proximity of the fiber surface.^{6, 7} Table 7-13 lists the measured tensile yield strength and calculated shear strength for the epoxy matrix as well as the S/AN/BA interphase composites. The anticipated matrix shear strength is 25 MPa. However, based on the maximum ILSS attained by the HPX-only composite, the matrix shear strength is closer to 15 MPa. This behavior is most likely connected with both the oxygen-containing reactive functionalities along the surface that shift the stoichiometry of the matrix cure, and the preferential diffusion to the fiber surface of one matrix component over the other.⁷ Thus, an interphase comprised of matrix material that is chemically and morphologically different from the bulk may exist in the HPX-only composite.

Table 7-13. The Tensile Yield Strength and the Shear Strength of the Matrix and Interphase Terpolymers Calculated According to the von Mises Criterion along with the ILSS of the S/AN/BA-grafted UHMPE/epoxy Composites.

<i>Material</i>	Yield Strength (MPa)	Shear Strength (MPa)	
		Calculated (von Mises)	ILSS
Epoxy resin (Tactix 123/D230)	43.5	25	—
S/AN/BA terpolymer:			
Low-Tg	0.0386	0.022	12.2
Mid-Tg	15.7	9.1	13.5
High-Tg	81.7	47	14.7

Table 7-13 also enumerates the shear strengths of the S/AN/BA terpolymers as well as the ILSS of the grafted UHMPE fiber-reinforced composites. If the S/AN/BA grafts formed discrete interphases, it would be reasonable to expect the ILSS values to correlate more closely with the terpolymer properties. Although it is unlikely that discrete interphases persist, the elevated temperatures (above the T_g 's of the interphase polymers) and the pressure associated with the compression molding processing conditions would likely permit some interdiffusion of the grafts and the matrix components. Moreover, the solubility parameters of the terpolymers and the matrix, calculated from group molar attraction constants, suggest that some intermolecular mixing is favored between the interphase grafts and matrix molecules (Table 7-14).⁸⁵ Thus, as the matrix cures, a semi-interpenetrating network would constitute the interphase. The mechanical response of the resulting interphase would involve a rule of mixture relationship between the terpolymer grafts and the matrix molecules interpenetrating the polymer interphase. Since the grafts and the matrix are not covalently bonded, the predominate interfacial failure mechanisms would include graft chain pullout either by disentanglement or matrix network scission, graft scission, or graft cleavage at the fiber surface.

The effect of grafting efficiency on the ILSS is indicated in Table 7-15. When the hydroperoxidation temperature is lowered 20°C, the ILSS decreases by over 20%, a statistically different ($\alpha = 0.05$) change compared with the Mid- T_g ($T_{HPX}=70^\circ\text{C}$) composite. However, this result further suggests that the grafting efficiency, although below the critical level for stress transfer with regard to bolstering the modulus, provides sufficient interaction to promote interfacial strengthening.

Table 7-14. Solubility parameters of the S/AN/BA terpolymers and the epoxy matrix calculated from group molar attraction constants.

Polymer (Feed Composition, mole%)	Predicted Solubility Parameter (cal cm ⁻³) ^{1/2} Poly(styrene) = 9.5 Poly(acrylonitrile) = 13.8 Poly(butyl acrylate) = 8.9
High Tg (23/44/33)	10.9
Mid Tg (13/29/58)	10.6
Low Tg (3/15/82)	9.6
DGEBA (Tactix 123)/D230 diamine resin	9.7

Table 7-15. Effect of Grafting Efficiency on the ILSS of Mid-Tg S/AN/BA-grafted UHMPE Fiber-reinforced Composites.

UHMPE Fiber Treatment	ILSS (MPa)
Washed	6.89 ± 0.49
Mid-Tg (T _{HPX} =50°C)	10.5 ± 0.4
Mid-Tg (T _{HPX} =70°C)	13.5 ± 0.7
HPX-only	14.6 ± 0.5

The preponderance of literature shows that conventional surface modification schemes generally lead to a decrease in the impact properties of most high performance fiber-reinforced composites, including the inherently tough UHMPE fibers. Table 2-3 shows numerous citations where this has been proven true. This adverse consequence is attributed to greater levels of adhesion, which prevent fiber pullout and fiber/matrix

debonding, the predominate mechanisms of energy dissipation in fibrous composites. However, the utilization of chemically grafted interphases provides additional mechanisms of energy dissipation associated with the graft/matrix intermolecular interactions.^{13, 73} These were expected to allow surface modification by grafting without a loss in the impact properties.

The impact strength of the UHMPE fiber-reinforced composites are listed in Table 7-16. As the interphase properties, i.e., modulus and strength, increase, so do the impact strength values. Surprisingly, the impact strength follows the trend in the ILSS for the various fiber treatments. This was an unexpected result since the High-Tg and HPX-only seemingly represented brittle interphases that presumably would diminish the energy absorbing properties of the composites. However, as described above, the HPX-only composite apparently is surrounded by matrix material with properties different from the bulk; possibly a ductile interphase, and the terpolymer interphases are more accurately represented by a mixture of the terpolymer and the matrix components. The important observation is that both the adhesion properties as well as the impact performance can be dramatically improved through fiber surface grafting. The increasing trend through the series, Washed, Low-Tg and Mid-Tg is not statistically significant ($\alpha = 0.05$) with each increment. However the Mid-Tg interphase represents a 26%, significant improvement over the Washed-fiber composites. Moreover, the High-Tg composite yields a 60% improvement compared with the Washed-fiber composites, and a 13% improvement over the HPX-only composites. These results contrast with the impact properties of oxygen-plasma treated UHMPE fiber composites tested by the same method (Table 7-17).¹³³

Table 7-16. Impact Strength of UHMPE Fiber-reinforced Composites.

UHMPE Fiber Treatment	Impact Strength (kJ/m ²)
Washed	75.9 ± 4.1
Low-Tg	86.5 ± 11.6
Mid-Tg	95.7 ± 7.5
HPX-only	109 ± 4
High-Tg	123 ± 1

Table 7-17. Impact Strength Decreases with Conventional Oxygen-plasma Treatment.

UHMPE Fiber Treatment	Impact Strength (kJ/m ²)
Untreated	60
Plasma treated	45

The effect of grafting efficiency on the impact properties are shown in Table 7-18. While the Mid Tg ($T_{HPX}=50^{\circ}\text{C}$) composite doesn't show a significant improvement over the Washed-fiber composites, a greater grafting efficiency affords a 16% improvement in the impact strength. This result is anticipated since a greater concentration of the graft chains would magnify the contribution of interfacial failure mechanisms involving the grafts.

Table 7-18. Effect of grafting efficiency on the impact strength of UHMPE/Epoxy composites.

Fiber Treatment	Impact Strength (kJ/m ²)
Washed	75.9 ± 4.1
Mid-Tg-grafted (Low Efficiency)	82.7 ± 1.5
Mid Tg-grafted (High Efficiency)	95.7 ± 7.5
HPX-only	109 ± 4

Conclusions

A promising aspect of surface modification technology is the possibility of using grafted polymer chains on fibers and fillers to improve the composite toughness as well as adhesion. The chemical bond between the graft and the fiber is integral to the strength-related properties of the interphase. However, a grafted chain can also undergo several molecular processes that toughen the interface, including chain pullout, scission, and disentanglement. These mechanisms contribute significantly to the energy dissipation of a propagating crack.^{13, 73} Therefore, the possibility of surface grafting treatments that yield both adhesion improvements and enhanced impact performance is feasible and ongoing.

There are, generally speaking, two methods of grafting, (i) attachment and (ii) growth of polymer chains from the surface of the reinforcement fiber. The attachment technique is more ubiquitous with modified glass and carbon fibers because of the high concentrations of reactive species at the surface. End-terminated polymers can subsequently be attached through a chemical reaction between the fiber surface-active species and the graft-polymer termination groups. However, the maximum graft attachment density achievable by this approach decreases with increasing degree of polymerization. The implication of this trade-off is that a maximum graft molar mass exists at which the graft areal density is sufficient to provide a toughening effect.^{13, 70, 71, 73}

One of the more promising, less chemically rigorous and hence more commercially viable methods of grafting, involves activation of the surface to yield initiation sites for grafting by addition-polymerization. The advantages of this growth-type, one-step grafting process include the control of chemical composition, end-group functionality, molar mass, polydispersity and the inherently higher areal densities achievable, compared with the attachment method of grafting for the same graft molar mass.

A growth-type method of surface-grafting for UHMPE fibers that is an extension of a technique reported by George and Willis was developed.⁷⁴ It involves a hydroperoxide initiation mechanism that provides grafting by a free radical-type polymerization. In this work, the capability to tailor the interphase properties by adjusting the composition of the graft polymer was demonstrated. Three S/AN/BA interphase terpolymers were synthesized with varying Tg and modulus and yield strength. A three phase, elastic shear lag model incorporating the interphase was used to establish the targeted interphase terpolymer compositions and properties. Three interphases were subsequently engineered; one with a low modulus and rubbery characteristics, the other a ductile, tough response and the last exhibiting a glassy modulus and brittle mechanical response. These were designated Low-Tg, Mid-Tg and High-Tg interphases, respectively. These were compared with the hydroperoxidized-only (HPX-only) and Washed fibers in terms of reinforcement and impact properties. The results showed that S/AN/BA-grafted interphases provide a significant reinforcing effect, even greater than the oxidative HPX-only treatment. In particular, the High-Tg interphase improves the adhesion properties of UHMPE fibers significantly, as demonstrated by the remarkable 110% increase in the ILSS. This translates into considerable improvements in the flexural properties of High-

Tg interphase composites including 37%, 60%, 30% and 95% increases in the modulus, proportional stress and deflection and the stress at 5 mm deflection, respectively. Although these kinds of achievements are realizable using a host of other surface treatments, this work demonstrates that the properties could be tailored by varying the graft chemical composition. Hence, a whole range of interfacial and composite properties is possible through control of the graft polymer composition. The ILSS, for instance, was increased in 10% increments through the series of interphases, Low-Tg, Mid-Tg and High-Tg. Likewise, the other mechanical properties and impact strength were adjusted through interphase selection. And unlike conventional oxygen-plasma treatments, e.g., the commercially available plasma treatment, where the adhesion gains are achieved at the expense of impact properties, the S/AN/BA interphases provide synergism between the reinforcement and impact properties.

The effect of grafting efficiency, i.e. graft attachment density, was assessed by changing the hydroperoxidation temperature. When the hydroperoxidation temperature is raised 20°, from 50°C to 70°C, the measured grafting efficiency, as determined from ESCA analysis of the nitrogen surface concentration, increases 50% from a graft fraction of 0.16 to 0.25. These values are low compared to that reported in Chapter 6. It might be possible to increase the grafting efficiency using a solvent other than benzene during the hydroperoxidation treatment. The color formation during this step is probably indicative of stable radical formation of benzene and styrene molecules. Hence, these radicals do not participate in the surface modification process. Mattson *et al.* showed that when chlorobenzene was substituted for xylene solvent, the solution grafting efficiency was

improved.⁷⁵ Thus, this adverse effect might be mitigated by the use of a solvent such as chlorobenzene.

A higher concentration of grafts enhances the ILSS, proportional stress and the stress at 5 mm deflection by more than 30%. Surprisingly, the modulus decreases to the value of the Washed-fiber composite when the graft fraction is less than 0.25. Thus, a critical graft attachment density exists at which an improvement in the stress transfer characteristics and modulus are possible. The graft efficiency also influences the impact properties of the UHMPE-fiber composites. When the graft efficiency is increased, a 16% enhancement in the impact strength is realized. This result is anticipated since a greater concentration of the graft chains magnifies the contribution of interfacial failure mechanisms involving the grafts.

Finally, a method of growth-type grafting has been developed and employed to engineer interphases with designed mechanical characteristics. The role of the interphase mechanics as well as the grafting efficiency on the composite mechanical properties has been further elucidated. It is now possible to extend this method to explore different aspects of surface grafting such as the effect of molar mass and end-group functionality using chain transfer agents, and ultimately, develop a better understanding of three phase composite materials.

CHAPTER 8 CONCLUDING REMARKS

Implications of the Research

Surface modification of polymers is well documented, and the extension of techniques such as plasma modification and UV-radiation induced grafting to polymeric fibers has been explored extensively. However, many of these methods cause severe surface damage and a corresponding reduction in the fiber mechanical properties. In this work, surface grafting of poly(butyl acrylate) ($T_g = -45^{\circ}\text{C}$) and poly(cyclohexyl methacrylate) ($T_g = 84^{\circ}\text{C}$) along the surface of UHMPE fibers has been achieved using ^{60}Co gamma irradiation at a relatively low dose rate and low total dose. This technique achieves surface grafting with complete retention of the exceptional UHMPE fiber mechanical properties. In addition, the stiff, PCHM grafts provided better stress transfer characteristics than the rubbery PBA grafts in the S/BA/CHM terpolymer and polystyrene-matrix composites. In particular, a 30% increase in strength and modulus was observed for PCHM-grafted fibers. On the other hand, PBA-grafted fibers induced void formation, i.e., energy dissipation through plastic deformation and volume expansion, at the fiber/matrix interface during deformation of terpolymer composites. The latter is manifest by a 75% increase in the elongation to failure and a concomitant 100% increase in the tensile energy to break. Therefore, surface modification by ^{60}Co gamma irradiation is an effective, non-destructive grafting method. Moreover, the interphase properties can be

tailored through graft polymer selection, which is advantageous in terms of tailoring the composite response for specific end-use applications, e.g. maximum toughness or reinforcement.³³

The drawback of grafting methods that utilize a high-energy source is the resulting competition between chain scission, crosslinking and grafting inherent to these approaches. This adverse feature yields crosslinked (“hyper-branched”) grafts that are difficult to characterize, thus limiting the tailorability and the further elucidation of the interphase region and its role on composite performance. Unfortunately, this aspect pervades the gamma-radiation grafting technique. Consequently, the hydroperoxidation grafting method was developed. This technique permitted the grafting of tethered, linear chains by a free radical-type polymerization.

This unique aspect was apparent when poly(styrene-*stat*-acrylonitrile)-grafted UHMPE fibers were analyzed using Tapping Mode AFM. The TMAFM images of the SAN-grafted UHMPE fibers showed a distinct topography comprised of uniformly distributed nodules that correlated well with a coil-like graft polymer conformation. Using a simple ‘hard-sphere’ model, the uniformly distributed nodules were attributed to individual SAN copolymer chains, each assuming a coil-like or mushroom-like conformation. The thickness of the grafted layer and the chain molar mass were subsequently estimated using random-coil statistics. At the lateral dimensions involved, no other imaging method exists that will provide this kind of information about the surface-limited grafts. In fact, these results corroborate the results of Austin *et al.* and the previous conclusion (see Chapter 6) that hydroperoxidation grafting yields linear chains tethered from the amorphous surface domains.⁴³

Hence, surface modification by hydroperoxidation also represents a non-destructive grafting method, and the utility of the technique has been successfully extended. In particular, the mechanical response and other physical properties of the interphase were tailored through comonomer selection of the interphase polymer. An advantage of this method of grafting is the simplicity and control afforded by the polymerization mechanism, e.g., choice of composition, chain transfer agents, temperature, etc. This aspect represents the key novelty of this technique with regard to surface modification of reinforcing fibers, and opens the door to a new generation of three-phase composite materials with new ranges of properties and performance.

The final section of this dissertation described the utilization of the hydroperoxidation grafting method for designed and synergistic interphases. This represents a new paradigm in the approach towards optimization of interfacial properties. Since the 1960's, there has been a substantial effort to produce thin interphases of elastomers on the surface of common reinforcements. The notion was that a thin, rubbery interlayer would contribute to an enhancement of composite toughness with minimal loss of strength and stiffness. The results were promising in terms of toughness and longitudinal strength and stiffness. However, the expanding use of composites under more complex loading geometries, and the fact that a majority of composite failures involve interfacial debonding, brought the interfacial properties to the forefront. Thus, a wave of surface treatments emerged that improved the adhesion characteristics, however generally at the expense of energy dissipation mechanisms and impact performance. This raised the question, "Is it possible to achieve both an enhancement in the energy absorption and reinforcement properties of composites?"

A truly synergistic interphase was previously unachieved because the use of grafted polymers at the interphase that are sufficiently stiff ($E > 100$ MPa) to allow adequate stress transfer between the fiber and matrix, and ductile enough to provide mechanisms for energy dissipation, were largely overlooked. Hence, this work represents a focused effort to design synergistic interphases. Using an elastic shear lag model, the effect of interphase modulus in a three-phase composite with a homogeneous, discrete interphase were modeled. Three interphases were subsequently selected and engineered; one with a low modulus and rubbery characteristics, the other a ductile, tough response and the last exhibiting a glassy modulus and brittle mechanical response. The interphases consisted of a statistical terpolymer of styrene, acrylonitrile and butyl acrylate monomers. The feed concentration of butyl acrylate was mainly adjusted to cover the range of properties. The three S/AN/BA terpolymer interphases were subsequently designated Low-Tg, Mid-Tg and High-Tg, respectively. These were compared with the hydroperoxidized-only (HPX-only) and Washed fibers in terms of reinforcement and impact properties. The Low-Tg and High-Tg interphases represented the status-quo approach. The use of rubbery interphases has been described. However rigid, reactive interlayer polymers are sometimes effectuated through selection of graft monomers containing pendant groups that are reactive with the matrix material, e.g., glycidyl methacrylate, acrylic acid, and allylamine with an epoxy matrix. This type of graft/matrix system results in a highly crosslinked interphase that is most likely brittle. The distinction between this type of interphase and the High-Tg interphase referred to here is that none of the S/AN/BA terpolymer grafts exhibited reactional functionalities capable of forming a covalent bond with the matrix.

The results showed that S/AN/BA-grafted terpolymer interphases provide a significant reinforcing effect, even greater than the oxidative HPX-only treatment. This was evident in terms of the modulus, proportional stress and elongation, stress at 5 mm deflection and the interlaminar shear strength (ILSS) of woven, bi-directional fiber-reinforced composites. Moreover, the properties were systematically tailored by adjusting the interphase properties or the grafting efficiency.

One of the realities when testing the level of adhesion of fiber-reinforced composites, e.g., by the ILSS method, is that the interfacial shear strength may be raised beyond that of the fiber shear strength. This is especially pertinent for the highly anisotropic UHMPE fibers. Peijs *et al.* concluded, for example, that increasing levels of fiber/matrix adhesion cause a change in the composite failure mode from debonding to cohesive fiber failure by longitudinal splitting.¹³⁴ This effect would be exacerbated by a reduction in the fiber tensile properties because of exposure to excessive temperatures, e.g., processing near the melting point of 140°C. Thus, the effect of annealing UHMPE fibers over a range of temperatures for two hours was evaluated. This annealing time corresponded with the length of cure given for the fiber-reinforced composites during the compression molding process. A ceiling temperature was identified, above which, the fiber properties begin to degrade. Hence, the composites were fabricated at 100°C in order to retain the excellent fiber properties and more fully ascertain the role of the interphase.

Peijs *et al.* also concluded that there exists a maximum attainable ILSS for UHMPE fibers by conventional plasma treatments.¹³⁴ This result suggests that a performance scale exists, along which the interfacial properties can be adjusted from poor

to a maximum value determined by the shear strength of the fiber itself. And since conventional surface treatments typically diminish impact resistance, the impact performance would decrease in the direction along which the adhesion increases. It was believed that this tradeoff between adhesion and toughness could be mitigated and possibly overcome using grafted interphases. In fact, the High-Tg terpolymer interphase yielded both a 110% and 95% improvement in the ILSS and flexural modulus, respectively, and a remarkable 60% increase in the impact strength. These results were previously unobtained. Moreover, the impact properties were incrementally improved through the series of, Low-Tg, Mid-Tg and High-Tg interphases, and by increasing the grafting efficiency. The latter result was anticipated since a greater concentration of the graft chains would magnify the contribution of interfacial failure mechanisms involving the grafts. Hence, the hydroperoxidation method was used to graft chains that promote stress transfer as well as energy dissipation mechanisms such as chain scission, disentanglement and crazing. Consequently, both tailored and synergistic responses were obtained in three-phase composites with designed interphases.

Future Directions

While this dissertation only considered growth-type mechanisms of grafting, there is a silent competition playing itself out between this method and the attachment-type method. The attachment method is more common with modified glass and carbon fibers because of the high concentrations of reactive species present at the surfaces of these fibers. End-terminated polymers can subsequently be attached through a chemical reaction between the fiber surface-active species and the graft-polymer termination groups.

However, the maximum graft attachment density achievable by this approach decreases with increasing degree of polymerization. The implication of this trade-off is that a maximum graft molar mass exists at which the graft areal density is sufficient to provide a toughening effect.

On the other hand, higher attachment densities are feasible utilizing the growth-type method of grafting since the tethering of chains relies on diffusion of monomer to the surface rather than polymer chains. However, the benefits of higher grafting densities is suspect since above a certain level, the tethered chains will assume a brush-like, impenetrable interphase that doesn't provide a toughening effect.⁷⁰ The determination of the most effective method will require further elucidation of the grafting mechanisms, surface morphology, graft conformation, attachment density and mechanisms of adhesion and energy dissipation. And the molecular-scale events under consideration will also necessitate continued development of more sophisticated characterization tools and experimental designs.

Atomic force microscopy (AFM) is a relatively new surface-imaging technique developed to give real-space information about the surface of a material on the atomic level. This technique allows designers to probe the surface on a nano-scale and image the surface morphology of grafts that were previously only modeled by Aubouy *et al.*⁶⁹ AFM can now be used to image the geometry and mechanics of the interphase for more sophisticated three-phase composite models.

Chain transfer agents can be combined with the hydroperoxidation grafting method to systematically vary the molar mass. Although the effect of molar mass has been ascertained by the attachment method, these polymers are all nearly monodisperse. Lin *et*

al. have hypothesized that polydisperse chains enhance adhesion because of the accessibility of longer chain ends and tails.⁷⁰ Hence, chain transfer agents also permit the study of polydisperse grafts with varying molar mass.

The prospect of self-healing composites is more realistic now that controlled, polydisperse grafts are viable. The effectiveness of low molar mass chains in crack-healing and craze-healing processes of homopolymers has already been substantiated.¹³⁵

Finally, chain transfer agents can also be used to end-functionalize growing chains. Depending on the chain transfer agent chosen, interphases that are chemically reacted to both the fiber and matrix, but not crosslinked, are feasible.

In summary, the development of controlled, well-defined interphases will permit a more thorough understanding of the role of the interphase in composites. Ultimately, these developments should begin to permeate commercial systems and expand the applications and performance ranges of composites.

APPENDIX
COMMON ABBREVIATIONS AND ACRONYMS

AAM-acrylamide

AFM-atomic force microscopy

AIBN-azobisisobutyronitrile

AN-acrylonitrile

ASTM-American Society for Testing and Materials

ATR/FTIR-attenuated total reflectance/fourier transform infrared spectroscopy

BA-butyl acrylate

CHM-cyclohexyl methacrylate

CTE-coefficient of thermal expansion

DGEBA-diglycidyl ether of bisphenol A

ΔH_m -enthalpy of melting

DMS-dynamic mechanical spectrometry

DSC-differential scanning calorimetry

E-beam-electron beam

ESCA-electron spectroscopy for chemical analysis

FTIR-fourier transform infrared spectroscopy

FTIR/PAS-fourier transform infrared spectroscopy/photoacoustic spectroscopy

GMA-glycidyl methacrylate

GPC-gel permeation chromatography

HDPE-high density polyethylene

HPX-hydroperoxidation

IFSS-interfacial shear strength

ILSS-interlaminar shear strength

MB-microbond test

MeOH-methanol

MMD-molar mass distribution

NMR-nuclear magnetic resonance

PBA-poly(butyl acrylate)

PC-poly(carbonate)

PCHM-poly(cyclohexyl methacrylate)

PE-poly(ethylene)

PEMA-poly(ethyl methacrylate)

PMC-polymer matrix composite

PMMA-poly(methyl methacrylate)

ppm-parts per million

PPS-poly(phenylene sulfide)

PS-poly(styrene)

PSf-polysulfone

PT-plasma treated

PVP-poly(2-vinyl pyridine)

rf plasma-radio frequency plasma

SAN-poly(styrene-stat-acrylonitrile)

S/AN/BA-poly(styrene-stat-acrylonitrile-stat-butyl acrylate)

SAXS-small angle x-ray scattering

S/BA/CHM-poly(styrene-stat-butyl acrylate-stat-cyclohexyl methacrylate)

SEM-scanning electron microscopy

TEB-tensile energy to break

T_g-glass transition temperature

TG/DTA-thermogravimetry/differential thermal analysis

THF-tetrahydrofuran

T_m-melting temperature

TMAFM-TappingMode™ atomic force microscopy

TTM-taut tie molecule

UHMPE-ultra high modulus polyethylene

UV-ultraviolet

UV/VIS-ultraviolet/visible spectroscopy

v_r-volume fraction

WAXD-wide angle x-ray diffraction

WBL-weak boundary layer

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BIOGRAPHICAL SKETCH

Jesse J. Arnold is the elder child of Judson and Georgia Arnold, born in Charleston, South Carolina, in June, 1970. After moving to Virginia then Oklahoma and back to Virginia, he began his secondary education in the Fairfax County School System in Alexandria, Virginia. Upon graduating from Hayfield Secondary School in 1988, he enrolled in the Virginia Polytechnic Institute and State University where he obtained his Bachelor of Science degree, magna cum laude, in materials engineering in 1992. He proceeded to the University of Florida under the tutelage of Dr. Anthony Brennan in the Department of Materials Science and Engineering. He was married to Jesyca on August 6, 1994. Jesse has one sister, Erin, who is eight years his younger. He has enjoyed athletics all his life and has spent most of his time outdoors, either playing organized sports or inventing games along the way. Currently, he enjoys playing golf, reading (especially Pat Conroy), spending time with friends and family, and traveling. Upon completion of the Ph.D., Jesse will embark on a career with Michelin Tire Company in Greenville, South Carolina.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Anthony B. Brennan, Chairman
Associate Professor of Materials Science
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



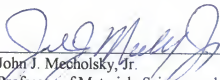
Christopher D. Batich
Professor of Materials Science and
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1997



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